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REMOVAL OF TRIHALOMETHANE PRECURSORS IN DRINKING WATER TREATMENT PROCESSES

Dissertation

Submitted to the Faculty of Graduate Studies and Research through the

Department of Civil and Environmental Engineering

In Partial Fulfillment of the Requirements for the Degree of:

Doctor of Philosophy

at the

University of Windsor

by

María Teresa Alarcón Herrera

Windsor, Ontario, Canada.

1994

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ABSTRACT

In this study the removal efficiency of humic substances by conventional drinking water treatment processes was studied in a full scale operating plant in Windsor, Ontario, Canada over a period of 16 months. A comparison of the removal efficiency of humic substances between conventional and advanced treatment processes such as ozonation (used as an oxidant before filtration) and the addition of *granular activated carbon* (GAC) was also carried out for the same water source (Detroit River) in a pilot scale treatment plant at the same location. The performance of different treatment processes in removing humic substances was evaluated through the quantification of humic substances and their *apparent molecular size distributions* (AMSD) in samples taken from the raw water and after each treatment process. The *dissolved organic carbon* (DOC) and the concentration of the non-humic substances for the water source (Detroit River) were also determined.

Results indicate that seasonal variations in humic substances concentration occurred, showing a maximum level during the month of April when the spring turn-over of water bodies took place. These seasonal variations were associated with the corresponding changes in THM concentrations observed during the same period. The fulvic and humic acid composition of humic substances and their *THM formation potential* (THMFP) were quantified. Their AMSD were determined by the *gel permeation chromatography* (GPC) and the *high performance size exclusion chromatography* (HPSEC). The humic substances from the Detroit River were found to be less reactive

in forming THMs ($\mu\text{g THM/mg C}$) when compared with the standard humic substances provided by the *International Humic Substances Society* (IHSS).

Coagulation-sedimentation was the most efficient process of the conventional treatment options in the removal of humic substances. The GAC greatly improved the removal efficiency of not only the humic substances but also of a large fraction of the non-humic substances. The removal of humic substances by the use of ozone as an oxidant before filtration was similar to that obtained by the conventional treatment with prechlorination.

The THMFP was determined on water samples from different processes and on their corresponding non-humic fractions. Precursor removal after each process effectively reduced the THMFP in the treated water. The non-humic fractions appeared to be potential contributors to the formation of THMs for high chlorine dosages.

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NOMENCLATURE

A_s	=	Integrated abundance for the selected ion for the internal standard	counts
A_x	=	Integrated abundance of the selected ion for the trihalomethane standard	counts
A_y	=	Integrated ion abundance of the primary characteristic ion of the sample analyte	counts
C_x	=	Analyte concentration	$\mu\text{g/L}$
k'	=	Column-capacity factor	
Q_s	=	Quantity of internal standard added	μg
Q_x	=	Quantity of trihalomethane standard	μg
RF	=	Response factor	
V	=	Purged sample volume	L
V_e	=	Elution volume	mL
V_{EL}	=	Volume of sample applied	mL
V_o	=	Void volume of the column	mL

GLOSSARY

AMM	=	Apparent Molecular Mass
AMS	=	Apparent Molecular Size
AMSD	=	Apparent Molecular Size Distribution
CWWA	=	Canadian Water Works Association
DCAA	=	Dichloroacetic Acid
DOC	=	Dissolved Organic Carbon
DOM	=	Dissolved Organic Matter
ECP	=	Extracellular Products
GAC	=	Granular Activated Carbon
GC	=	Gas Chromatography
GPC	=	Gel Permeation Chromatography
HPLC	=	High Pressure Liquid Chromatography
HPSEC	=	High Performance Size Exclusion Chromatography
IHSS	=	International Humic Substances Society
MCL	=	Maximum Contaminant Limit
MOE	=	Ontario Ministry of Environment
MOEE	=	Ontario Ministry of Environment and Energy
MS	=	Molecular Size
MSD	=	Mass Selective Detector
NOM	=	Natural Organic Matter
NORS	=	National Organics Reconnaissance Survey of Halogenated Organics
NP _{TOX}	=	Non Purgable Total Organic Halide
NVTOC	=	Non Volatile Total Organic Carbon
PAC	=	Powdered Activated Carbon
RO	=	Reverse Osmosis
TCAA	=	Trichloroacetic Acid

THM(ins)	=	Instantaneous Trihalomethanes
THMFP	=	Trihalomethane Formation Potential
THMs	=	Trihalomethanes
THMs(term)	=	Terminal Trihalomethanes
TOC	=	Total Organic Carbon
TOX	=	Total Organic Halides
UF	=	Ultrafiltration
USEPA	=	United States Environmental Protection Agency
UV	=	Ultraviolet Light
UVA	=	Ultraviolet Absorbance
WHO	=	World Health Organization
WWTP	=	Windsor Water Treatment Plant

Chapter I

INTRODUCTION

1.1. Background

Trihalomethanes (THMs) are chlorinated organic compounds produced in drinking water treatment by the reaction of aqueous chlorine with organic carbon . The source of organic carbon may be naturally-occurring plant and animal decay products (aquatic humic substances), algal extracellular products, agricultural run-off and chemical pollutants which may be present in the water. The most commonly produced THMs in water chlorination are chloroform (CHCl_3), dichlorobromomethane (CHCl_2Br), dibromochloromethane (CHClBr_2) and bromoform (CHBr_3).

The THMs in drinking water have come under investigation since 1974 when Rook (1974) and Bellar and Lichtenberg (1974) reported the possible occurrence of significant amounts of THMs in drinking waters. Studies carried out in the USA by the *Environmental Protection Agency* (EPA) showed and confirmed the widespread occurrence of THMs in chlorinated water supplies (Symons *et al.*, 1975). These compounds are suspected carcinogens, and in 1976, the National Cancer Institute in the United States (NCI, 1976) demonstrated that chloroform caused cancer in laboratory mice and rats. Based upon these observations, the United States Environmental Protection Agency (USEPA) established a limit of 0.1 mg/L of total THMs in 1979 (USEPA, 1979). In 1990, the USEPA classified the first three compounds (CHCl_3 , CHCl_2Br and CHClBr_2) as belonging to Cancer group B₂ (probable human carcinogen)

and the last one (CHBr_3) in Cancer group C (possible human carcinogen) (Pontius, 1990). It is anticipated that the new *maximum contaminant limit* (MCL) for THMs will be between 80 and 40 $\mu\text{g/L}$ (Pontius, 1993). In Canada, the limit for total THMs in drinking water has been regulated at 350 $\mu\text{g/L}$. Several surveys for organics in drinking water were initiated in 1974 by the then *Ontario Ministry of Environment* (MOE). In these studies, haloforms were determined at 48 different water treatment plants throughout the province. Brantford was found to have the highest average chloroform concentration of 159 $\mu\text{g/L}$ (MOE, 1977). Since 1985, through the Drinking Water Surveillance Program, the *Ontario Ministry of Environment and Energy* (MOEE) has analyzed and compiled data from municipal water plants across the province. This program provided useful information on drinking water quality, particularly on the occurrence of THMs in drinking water. It was observed that during the years 1985-1986 in the City of Windsor, all the THM values exceeded the newly proposed Canadian limit of 50 $\mu\text{g/L}$ (CWWA, 1992). The average concentration reported was 69 $\mu\text{g/L}$. From 1987 to 1988, the average concentration was 52 $\mu\text{g/L}$ (MOE, 1985-1988). Henshaw *et al.*, (1993) analyzed the occurrence of THMs in drinking water from the Great Lakes and found that the communities of Thunder Bay and Windsor exceeded the *World Health Organization* (WHO) guideline of 30 $\mu\text{g/L}$ for chloroform. These cities exceeded the WHO guideline 70% and 40% of the time respectively, during the years 1986 to 1990.

1.2. THM Precursors

Aquatic humic substances, constituting most of the naturally occurring organic matter in water supplies, account for approximately 30 to 50% of the DOC in most natural waters and have been shown to be the most important precursors in THM formation (Rook, 1976; Stevens *et al.*, 1976; Thurman, 1985).

Humic substances in natural waters are complex mixtures of organic matter. They are described as a general category of naturally-occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow to black in colour, of high molecular size, and refractory (Aiken *et al.*, 1985).

The nature of aquatic humic substances and their complex character vary seasonally and with geographic location. This can be an important factor in influencing the performance of the water treatment processes and in the formation of the THMs upon chlorination.

1.3. THM Control

Reduction of the concentration of THMs in a water supply may be accomplished by one, or a combination, of the following schemes:

- ▶ removal of the THM precursors;
- ▶ removal of the THMs after their formation;
- ▶ use of disinfectants other than chlorine.

Although each of these practices has advantages and disadvantages, precursor removal through the removal of organic matter is considered to be the most beneficial

(Rook, 1976; Kavanaugh, 1978; Weber and Jodellah, 1985). This approach, in addition to the reduction of THM concentration, may help reduce other treatment problems associated with the presence of natural organics. Such problems include: increased chlorine demand, higher coagulant dosages, fouling of ion exchange membranes or resins, colour, taste and odour.

Several treatment processes can be used to reduce the organic content of raw water. Processes such as coagulation, adsorption by GAC, chemical oxidation, ion exchange and ultrafiltration are considered effective in this regard. Process selection depends on the characteristics of the water to be treated and operational and economic factors. Coagulation in conventional treatment processes constitutes the first step in the removal of organic matter. However, in many cases, coagulation alone may not be capable of removing enough precursors to meet the proposed THM standards. Thus, advanced treatment processes may have to be used (Stevens *et al.*, 1976; Lange and Kawczynski, 1978; Lykins *et al.*, 1987).

Among these processes, adsorption by GAC is known to be a very effective method in the removal of not only THM precursors and THMs themselves, but also in the removal of taste and odour and a number of toxic and carcinogen compounds (Weber and Bernardin, 1987; DiGiano, 1987). Ozone is both a powerful oxidant and disinfectant. Because of the need in many cases for a strong oxidant and primary disinfectant to replace chlorine for pretreatment, interest in ozonation as a precursor removal has also increased in the last decade (Singer and Chang, 1989).

The removal of humic substances by drinking water treatment processes reduces

the concentration of THMs in the treated water. Several studies have been conducted to determine the influence of humic substances on the efficiency of various treatment processes for the control of THMs (Babcock and Singer, 1979; McCreary and Snoeyink, 1980; Collins *et al.*, 1985; Chadik and Amy, 1987; Vik and Eikebrokk, 1989; Lykins and Clark, 1989). In these studies, it has been observed that similar treatment processes usually show different results depending on the source-specific characteristics of the humic substances present in the raw water. One of the important characteristics of the humic substances associated with the removal efficiency of the different treatment processes is the molecular size (Collins *et al.*, 1985; Weber and Jodellah, 1985; Sinsabaugh *et al.*, 1986; Chadik and Amy, 1987). It was observed in the literature that certain processes are more effective in removing only specific molecular size fractions (Edzwald, 1987; El-Rehaili and Weber, 1987; Chadik and Amy, 1987 and Amy *et al.*, 1992). However, most of these studies were done either in a laboratory or were based on the results of a single sample from conventional treatment plants. Therefore, there are insufficient data available on the performance of the treatment processes in removing different fractions of humic substances.

The concentration and properties of humic substances are some of the most important characteristics of the water-source that play a significant role in the reduction of THMs in water treatment processes. Since this information is not available for the Detroit River, a major water source for several communities in Ontario, it was decided to determine its humic substance content and their fate along various water treatment processes over a period of 16 months. Based on the above, the present study was

undertaken, where samples were collected and analyzed from

- ▶ a full scale conventional water treatment plant with prechlorination, coagulation-sedimentation, filtration and postchlorination;
- ▶ a pilot plant with conventional treatment followed by GAC (advanced treatment);
- ▶ a pilot plant with ozonation before filtration followed by GAC (advanced treatment);

All of the above plants are located in Windsor, Ontario, Canada.

1.4. Objectives

The specific objectives of this research were to:

- ▶ identify the AMSD and seasonal variation of the natural organic precursors of trihalomethanes (humic substances) in the Detroit River;
- ▶ determine the AMSD range of humic substances removed by conventional treatment in the full scale plant;
- ▶ determine the relationship between the THMFP and the following parameters: DOC, UVA and AMSD
- ▶ compare the removal efficiency of humic substances between conventional treatment and advanced treatment processes with ozonation before filtration and GAC.

Chapter II

LITERATURE REVIEW

2.1. Humic Substances

Humic substances comprise a general class of biogenic, refractory, yellow-black organic substances that are ubiquitous that occur in all terrestrial and aquatic environments (Aiken *et al.*, 1985). Humic substances produce the yellow-to-brown colour common to most surface waters. Several theories in the literature explain the presence of humic substances in natural water, but the mechanisms for the formation of aquatic humic substances are not known (Stevenson, 1982; Malcolm, 1985). Whether they are formed in the ground and then washed out or directly formed in the water itself, aquatic humic substances are the result of the microbiological, chemical and photochemical reactions that occur during the degradation and polymerization of vegetable matter.

Operationally, aquatic humic substances have been defined by Malcolm (1985) as the: "...portion of the organic substances in water which passes through a 0.45- μ m membrane filter and upon acidification to pH 2 with HCl, has a column distribution coefficient (k') greater than 50 on XAD-8 resin at 50% breakthrough of the colour for the visually dark-coloured, nonspecific amorphous carbonaceous material." They are non-volatile; their elemental composition is approximately 50 percent carbon, 4 to 5 percent hydrogen, 35 to 40 percent oxygen, 1 to 2 percent nitrogen and less than 1 percent for sulphur and phosphorous. The major functional groups include: carboxylic acids, phenolic hydroxyl, carbonyl, and hydroxyl groups (Thurman, 1985). Aquatic humic

substances are composed of aquatic fulvic acid and aquatic humic acid. They are named according to their solubility at different pH, as shown in Table 2.1 .

Table 2.1. Classification of aquatic humic substances.

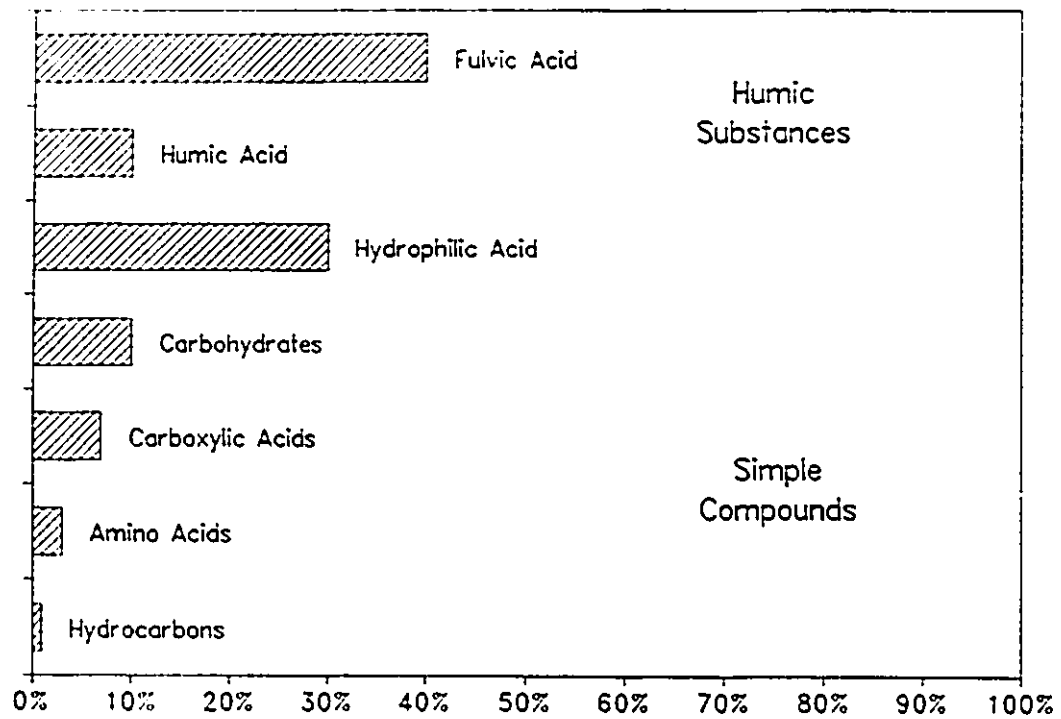
Group	Description
Humic acid	fraction of aquatic humic substances that is soluble at alkaline pH but precipitates at pH = 1
Fulvic acid	fraction of aquatic humic substances that is water soluble at alkaline pH and acidic pH

2.1.1. Humic Substances and their Distribution in Water

According to Thurman (1985) the *dissolved organic carbon* (DOC) in natural waters includes many types of organic compounds, which can be classified by abundance into three major groups: (i) humic substances, (ii) hydrophillic acids and (iii) simple compounds that include carboxylic acids, amino acids, carbohydrates and hydrocarbons. Figure 2.1 shows the distribution of these compounds in a typical river water with a DOC concentration of 5 mg/L.

The concentration of humic substances varies in different natural waters. The lowest concentrations of humic substances are in ground water and sea water (0.05 to 0.06 mg/L as C). Streams, rivers and lakes contain from 0.50 to 4 mg/L as C, and coloured rivers and lakes have much larger concentrations of humic substances, from 10 to 30 mg/L as C (Thurman, 1985). As a group, humic substances account for approximately 30 to 50 percent of the DOC in most natural waters, except in coloured waters, where they contribute 50 to 90 percent of the DOC. Figure 2.2 shows the

variation in concentration of humic substances for different waters.



Source: Thurman, 1985.

Figure 2.1. Distribution of dissolved organic compounds for typical river water with a DOC of 5 mg/L.

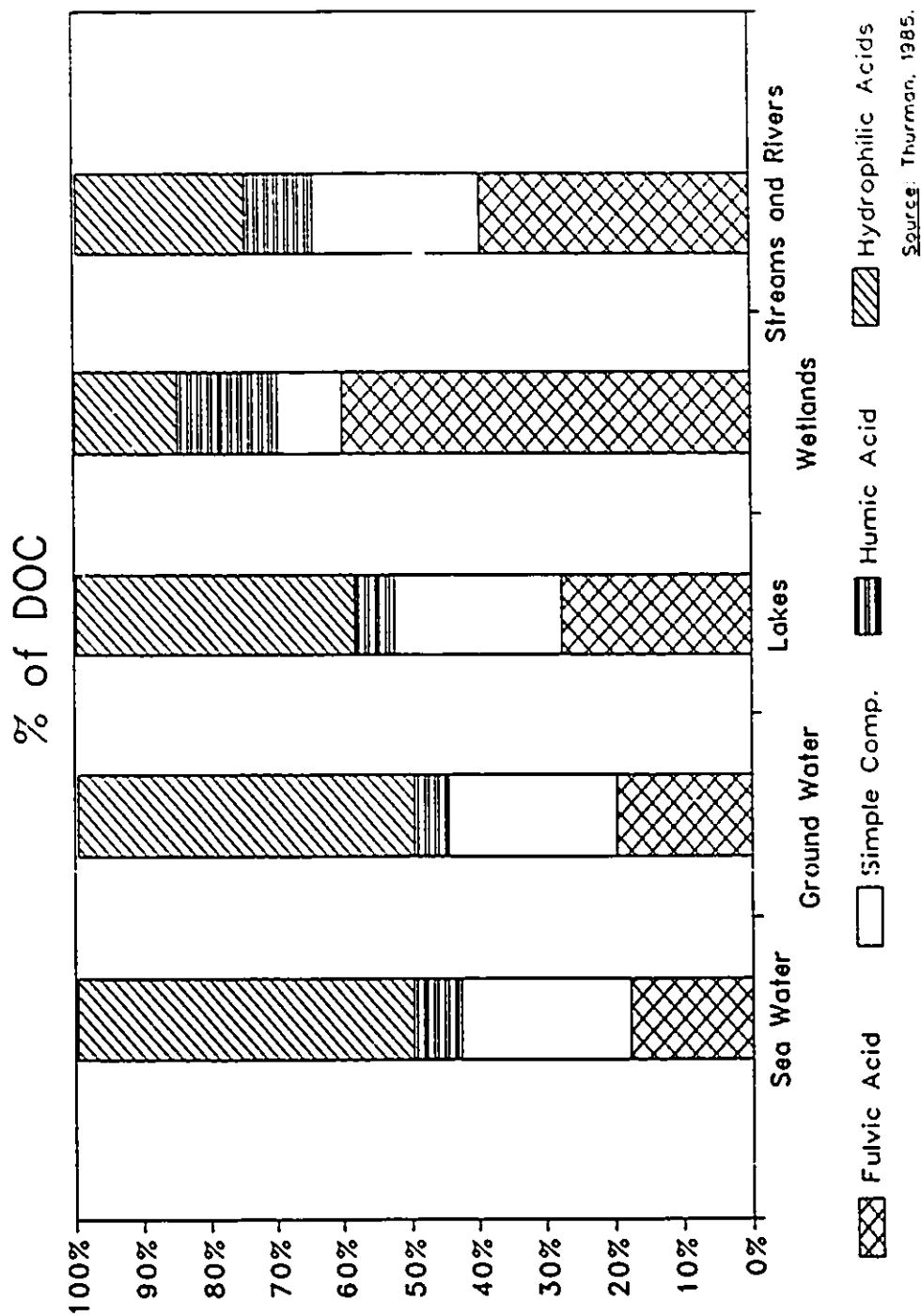


Figure 2.2. Humic substances concentration in different natural waters.

2.1.2. Characterization of Aquatic Humic Substances

Because an exact structure or family of structures cannot be written for humic substances, these must be characterized on the basis of several chemical and physical properties. The characterization recommended by soil researchers, (Aiken *et al.*, 1985) includes:

- ▶ DOC of the water sample from which humic substances were isolated
- ▶ percentage of the DOC as humic substances
- ▶ fulvic/humic acid
- ▶ method of isolation
- ▶ molecular size
- ▶ THMFP
- ▶ *total organic halide* (TOX)
- ▶ elemental analysis for carbon, hydrogen, oxygen, nitrogen, ash content
- ▶ functional group analysis
- ▶ ^{14}C age, ^{16}O / ^{18}O , proton NMR, amino acid composition, infrared spectra, pentose and hexose sugar composition.

In this dissertation, only the first six parameters were determined because of instrument limitations.

2.1.3. Methods of Isolation

Many techniques have been used for extracting humic substances from water. A summary of these techniques, showing the advantages and disadvantages, is presented in Table 2.2. It is obvious that there are so many methods available that comparisons between the results obtained cannot be easily made. For this reason, the IHSS makes available reference humic substances, isolated from the Suwannee River, near Fargo, Georgia (MacCarthy and Suffet, 1989). The Society also recommends a method of isolation, which is essentially the same as the one used by Thurman and Malcolm (1981). This method includes microfiltration of water and adsorption of organics on XAD-8 resin at pH 2, followed by sodium hydroxide elution. Since this method was used in the isolation of humic substances for this dissertation, a detailed description is given in Chapter IV.

2.1.4. Molecular Size

Molecular size is an important criterion for defining humic substances. Soil humic substances appear to have higher molecular sizes than the aquatic humic substances. The results of the molecular size measurements of humic substances are highly dependent on the method used, as well as pH, concentration and humic strength (Steelink, 1985).

There are a number of methods to measure molecular size including gel filtration, ultrafiltration (UF) and small-angle X-ray scattering. In these methods, model compounds of known molecular mass and composition are used to estimate the molecular mass of a humic substance. Problems can arise if the model compounds are not sufficiently

Table 2.2. Methods used to isolate and concentrate aquatic humic substances.

Method	Advantages	Disadvantages
Vacuum distillation	1. Low temperature	1. All solutes concentrated
Freeze-drying (Lyophilization)	1. Mild 2. High concentration factors 3. Sample taken to dryness	1. Method is slow 2. All solutes with exception of volatiles are concentrated
Freeze concentration	1. Mild 2. Inexpensive 3. Simple	1. Method is slow 2. All solutes concentrated
Coprecipitation	1. Inexpensive 2. Effective for high DOC waters	1. Efficiency dependent on initial DOC 2. Inefficient for large volumes. 3. Inorganic matter must be separated from inorganic salts.
Ultrafiltration	1. Organic solutes fractionated by molecular size	1. Interaction with membranes 2. Fouling of membranes
Reverse osmosis	1. Ambient conditions mild 2. Large volumes can be processed	1. All solutes concentrated 2. Efficiency dependent on concentration
Solvent extraction	1. Inorganic salts effectively excluded	1. Humic substances insoluble in many solvents 2. Method is slow
Anion exchange (Strong-base resins)	1. Method is simple 2. Large volumes can be processed 3. High capacities for macroporous resins	1. Irreversible sorption probable 2. Fouling of resin possible 3. Resin bleed 4. All anions concentrated
Non-ionic macroporous sorbents	1. Method is simple 2. Resins easily regenerated 3. Large volumes processed 4. High capacities 5. Efficient desorption of acrylic ester resins	1. Irreversible sorption possible on styrene divinylbenzene resins 2. Desorption with NaOH 3. Precautions required to prevent oxidation of humic substances 3. Resin bleed. 4. pH adjustment to pH 2 prior to adsorption

Source: Aiken *et al.*, 1985.

similar to the humic substances of interest. Choice of the appropriate model compound is frustrated by the lack of detailed information about the chemical structure of humic substances (Malcolm, 1985). The term *molecular mass* is commonly used in the literature to express the results obtained by methods that measure molecular size. However, given the unknown and complex character of humic substances, it will be more appropriate to use *molecular size* to relate the operational character of analytical techniques that actually characterize the size of molecules. The term *molecular mass* will be used in this dissertation only to refer to the literature review data in the way that different authors have done.

According to Wershaw and Aiken (1985), molecular mass values range from 500 for some aquatic humic substances to 10,000,000 for soil humic acids and there is little agreement between the various methods to determine these masses. Gjessing and Lee (1967) fractionated Norwegian waters by GPC and found a molecular mass range from less than 700 to greater than 200,000. They found discrete peaks in this molecular mass range and concluded that the main part of the organics in natural waters are fractionable and probably do not consist of continuous distributions of all masses of molecules. However, Swift and Posner (1971) stated that discrete peaks obtained in GPC were unlikely to reflect the actual molecular mass distribution of humic substances and the peaks found by Gjessing and Lee (1967) and others were the result of complex gel-solute interactions. They subsequently indicated that the elution curve that identified these peaks resulted from the combined effects of molecular mass, charge density and adsorptivity of the sample. They maintained that the continuous distribution around a single mean

value would be expected and was so found when certain chromatographic conditions were controlled to minimize gel-solute interaction.

Aiken (1984) has pointed out that UF techniques to determine molecular mass distribution must be interpreted carefully because the pore size in the membrane is often not uniform, breakthrough may occur at high concentrations, humic substances can interact with the membrane surfaces and the reaction of humic substances with other constituents can seriously affect the mass of the retained molecules.

Thurman *et al.*, (1982) used the small-angle X-ray scattering technique to determine the molecular mass of humic substances. They reported that this technology appeared to be the most accurate method for molecular mass determination to date, although the high cost of the necessary equipment to conduct this type of analysis may impede its use in most cases. They found that most aquatic material was dissolved fulvic acid and the molecular mass determined by this technique corresponded to a range of 500 to 2000. For humic acids, these researchers reported values in the range of 1,000 to greater than 10,000.

2.2. Trihalomethanes in Drinking Water

The THMs found in drinking water are members of the family of organohalogen compounds which are named derivatives of methane where three of the four hydrogen atoms have been replaced by three halogen atoms. THMs most commonly found in drinking water supplies are chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), dibromochloromethane (CHClBr_2) and bromoform (CHBr_3). Among these, chloroform

is generally the dominant halogenated product (Rook, 1974; Bellar and Lichtenberg, 1974; Stevens *et al.*, 1976)

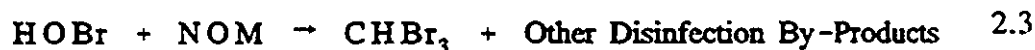
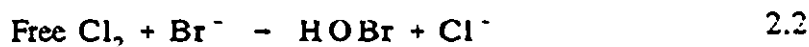
2.2.1. THM Formation

THM formation begins at the first point of chlorination and continues for days as the water passes through the distribution system. Measurement of THM levels at any point in the system varies as a function of time from the point of chlorination. *Natural organic matter* (NOM), consisting mainly of humic and fulvic acids, is the principal precursor of THMs in most waters and represents the major portion of the *total organic carbon* (TOC) content (Rook, 1974; Stevens *et al.*, 1976; Singer and Chang, 1989).

The formation of chloroform can be represented as follows:



In the presence of bromide ions, free chlorine readily oxidizes the bromide ion to hypobromous acid (HOBr), which can subsequently react with natural organic material to produce bromoform:



The combined action of both chlorine and hypobromous acid leads to the formation of the mixed chloro-/bromo-THMs species and other mixed halogenated by-products (Rook, 1977; Morris, 1977; Cooper *et al.*, 1985; Singer and Chang, 1989).

2.2.2. General Mechanisms

The mechanism of the THM-formation reaction as it occurs in the water treatment process is not known and has become a matter of investigation for many researchers including Rook, (1977); Dore *et al.*, (1982) and Reckhow, (1984). However, until now the complexity and lack of knowledge of the precursors (humic substances), has precluded the description of the reaction mechanisms. Many approaches have been taken by using different model compounds, many of them components of humic substance degradation, proteins and algae biomass.

Rook (1974) was the first to propose the classic haloform reaction of hypochlorous acid with acetone to be a possible pathway for the formation of chloroform. However, in 1977, Morris indicated that the kinetics of the classical haloform reaction of hypochlorous acid with acetone were too slow to be of importance in water treatment and that more highly activated structures than those of simple methyl ketones were required to account for haloform formation.

Rook in 1976 showed that methahydroxy aromatic compounds were particularly effective in the THM reaction. These compounds are some of the components of the fulvic acid structure. Further, it was stated that haloform production could not account for the chlorine demand observed in these experiments. It was pointed out that other volatile and non-volatile chlorinated or brominated organics were produced and that the concentration of non-volatile compounds may exceed those of THMs by a factor of 5 or more. These findings were supported later by many other researchers such as Norwood *et al.*, (1980); Coleman *et al.*, (1980); Liao *et al.*, (1982); Miller and Uden (1983);

Johnson and Jensen (1986) and Fielding and Horth (1986).

The application of powerful qualitative analytical techniques in the late 1970's and 1980's revealed a very complex range of chlorinated and brominated organic substances present in chlorinated water supplies. It became apparent that the bulk of these were synthesized during water treatment chlorination. Coleman *et al.*, (1980) identified 460 compounds in a tap water extracted from an Ohio drinking water sample. Field studies indicated that trichloroacetic acid (TCAA) was one of the dominant products among the *total organic halides* (TOX) produced from isolated humic material and in chlorinated raw water samples. It was reported that the sum of TCAA and chloroform accounted for about 50 percent of the TOX produced (Norwood *et al.*, 1986).

Stevens *et al.*, (1989) detected over 500 *disinfection by-products* (DBPs). Many of these were found at $\mu\text{g/L}$ levels although most were probably much lower and the majority were not identified. A survey of finished waters of ten U.S. cities confirmed the presence of $\mu\text{g/L}$ concentrations of several of these compounds. Johnson and Jensen (1986) while reporting on the THM and Total Organic Halides (TOX) formations, showed that TOX consisted of both the purgeable (THMs plus other volatile compounds), and non-purgeable (non-volatile compounds) fractions. Summarizing the work of various researchers (see Table 2.3), it was concluded that THMs were only the *tip of the iceberg*, a minor fraction from the TOX and the majority of compounds were the *non-purgeable chlorinated organics* (NPTOX). The latter fraction is also associated with the mutagenic character of chlorinated drinking water. Consequently, it has been suggested that one should consider not only the THMFP but also TOX concentrations in monitoring

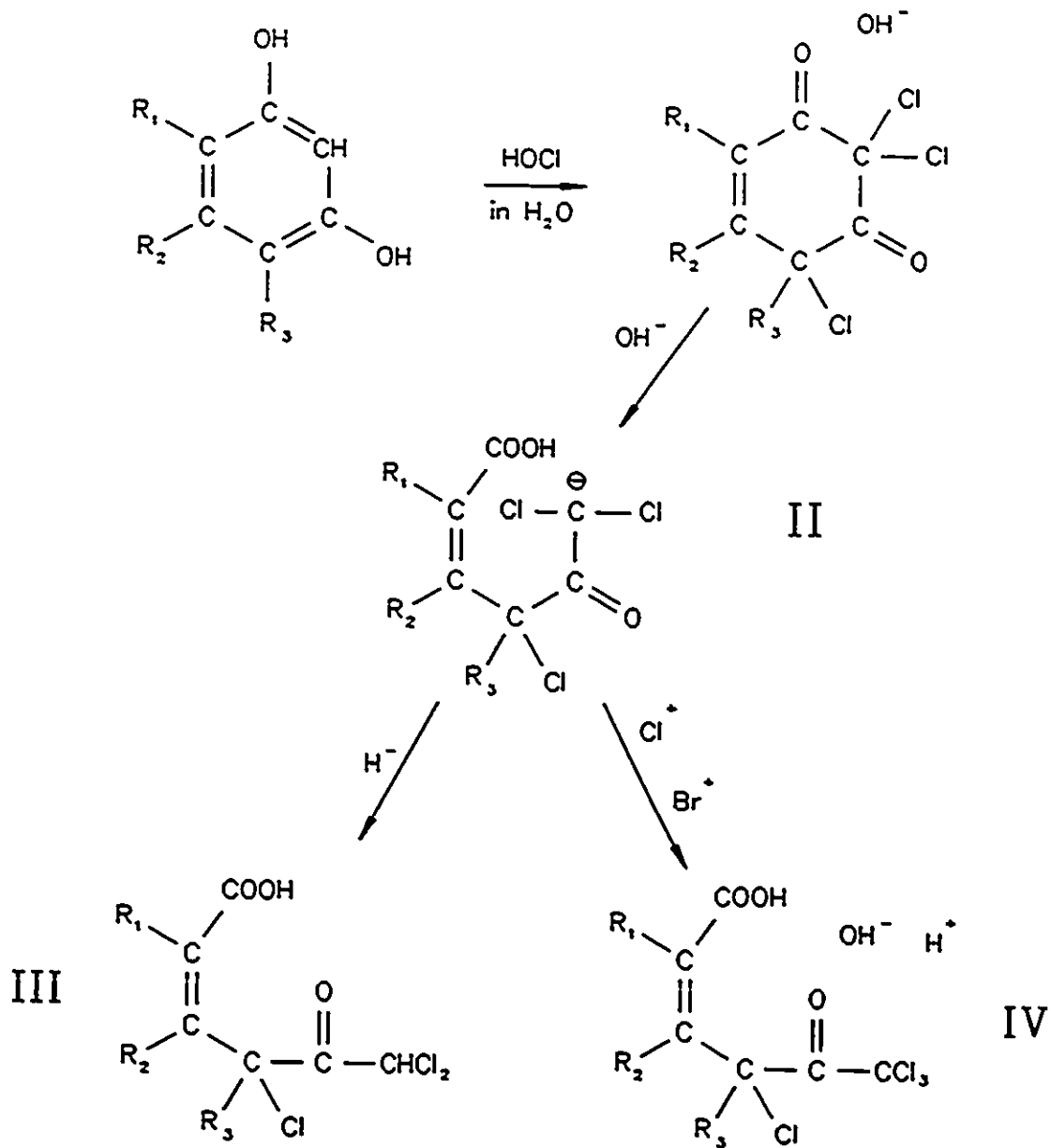
chlorination practices and in considering modifications to water treatment processes.

In 1977, Rook proposed a reaction mechanism for haloform formation from fulvic acid, where resorcinol is the active site. Figure 2.3 shows the proposed pathway, where the resorcinol-type moiety of fulvic acids may be substituted by R_1 , R_2 , R_3 . The haloform reaction initially will give the intermediate carbanion II, which is rapidly halogenated further to product IV, producing a trihalomethylated ketone which then decomposes to give chloroform, or alternatively protonated to III and stabilized.

Table 2.3. Significance of NPTOX compared with THMs.

Substrate	Conditions	Avg. NPTOX/THMs	Reference
Various humic, fulvic substances; groundwater; secondary effluent	pH = 7 TOC = 3 mg/L Cl ₂ dose = 2-100 mg/L t = 100 h	3.1 - 4.4	Fleischacker and Randtke (1983)
Various humic and fulvic substances	pH = 7 TOC = 5 mg/L Cl ₂ dose = 20 mg/L t = 72 h	3.3 - 4.4	Reckhow and Singer (1984)
Black Lake (N.C.), fulvic substances	pH = 7 TOC = 421 mg/L Cl ₂ dose = 2488 mg/L t = 24 h	4.8	Christman <i>et al.</i> , (1983)
Chlorophyll	pH = 7 TOC = 4.4 mg/L Cl ₂ dose = 20 mg/L t = 24 h	4.6	Wachter and Andelman (1984)
Soil, humic substances	pH = 6 TOC = 5.5 mg/L Cl ₂ dose = 10 mg/L	1.6	Quinn and Snoeyink (1980)
* Abbreviations: TOC = total organic carbon, t = reaction time			

Source: Johnson and Jensen, 1986.



Source: Rook, 1977.

Figure 2.3. Reaction mechanism for haloform production from fulvic acid.

Halogenated acetic acids have been observed to be chlorination products of many organic compounds (Rook, 1977 and Norwood *et al.*, 1986). Reckhow, (1984) has proposed a fulvic acid-chlorine reaction scheme in which the formation of transient beta-diketone type structures is a significant feature (see Figure 2.4). The activated carbon of the beta-diketone rapidly becomes fully substituted with chlorine. Hydrolysis will occur rapidly. If the remaining R group is $-OH$, then the reaction will stop at that point giving dichloroacetic acid (DCAA). Otherwise the structure would be further chlorinated to a base-hydrolysable trichloromethyl species.

Thompson (1989) proposed a general view of the progress of chlorination of humic substances after analyzing the volatile (purgeable) and some non-volatile chlorination by-products (extractable) of a single high humic content natural water and the fulvic acid derived therefrom. Figure 2.5 shows a schematic view of the proposed pathways. The production of non-chlorinated aliphatic and aromatic by-products from humic substances results from the oxidation of humic substances by chlorine. Chlorinated aliphatic acids were observed as the predominant chlorinated by-products. He proposed the placement of the mutagenics E-MX (E-2-chloro-3(dichloromethyl)-4-oxo-butanoic acid) and MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2(5h)-furanone) in the overall chlorination scheme.

2.2.3. Factors Affecting THM Formation

While the actual mechanism of THM formation may not be fully understood, the following factors have been identified as affecting the reaction:

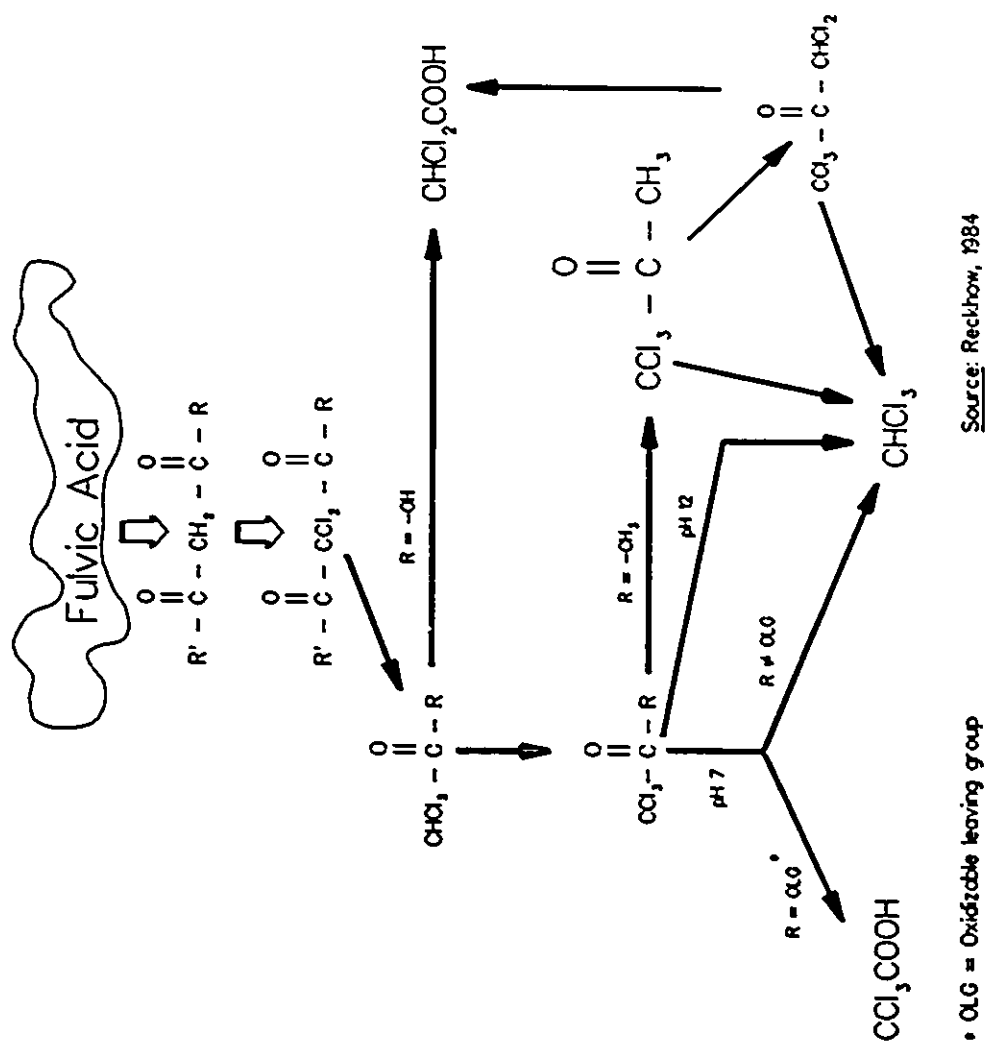
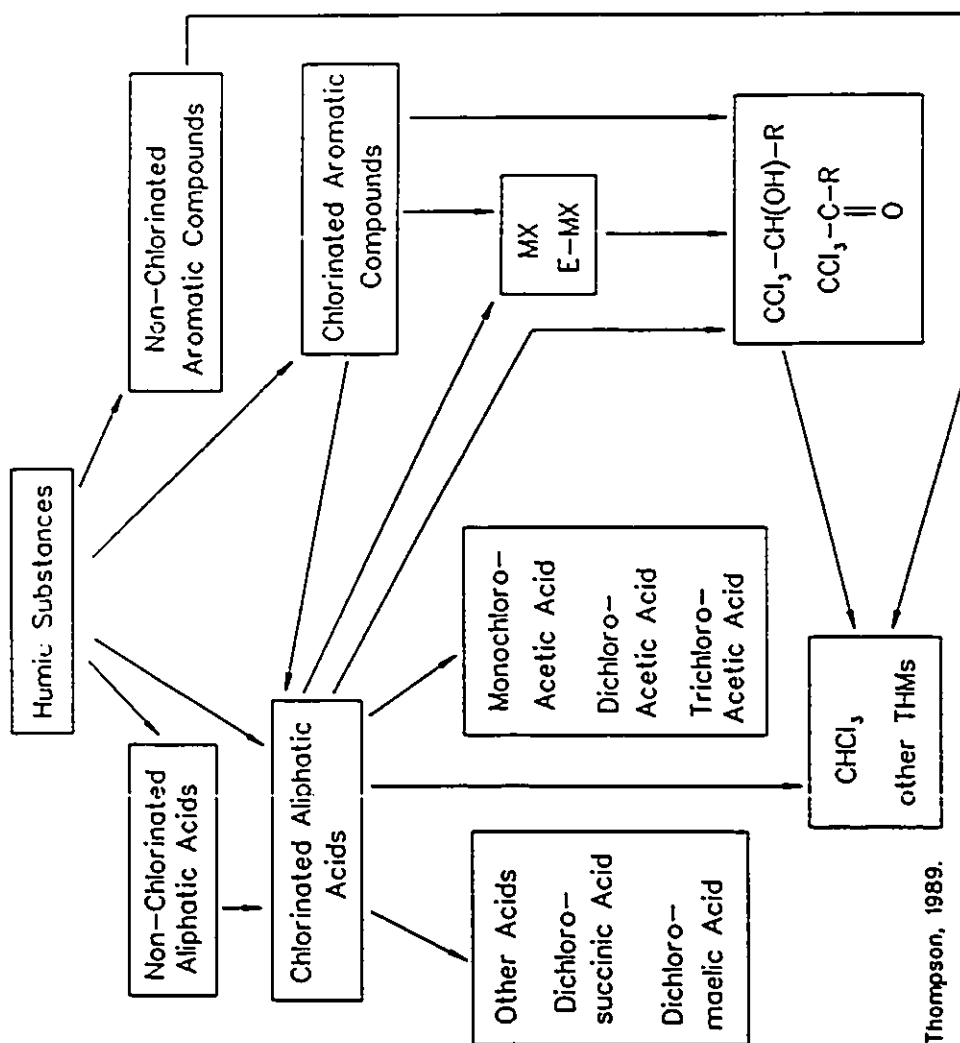


Figure 2.4. Proposed mechanism for the formation of organic halide products from fulvic acid.



Source: Thompson, 1989.

Figure 2.5. General view of the progress of chlorination.

- ▶ pH
- ▶ temperature
- ▶ reaction time
- ▶ chlorine dose and chlorine demand
- ▶ bromide ion concentration
- ▶ nature and concentration of the precursor.

2.2.3.1. pH

A number of studies have found pH to be a very important parameter in determining THM formation. The increase in THM formation when pH was increased from 7 to 11 was found to be 40% and 50%, depending on the organic source and chlorination condition (Oliver, 1978 and Oliver and Lawrence, 1979, respectively). Stevens *et al.*, (1976) reported that the THM formation from humic acid increased as pH was increased from 5.2 to 9.2, and that at pH of 3.4, THM formation was virtually the same as at a pH of 5.2. Boyce and Horning (1983) reported a maximum THM formation from terrestrial humic acids at pH 10 with a significantly diminished formation below pH 6 and above pH 12.

Oliver (1980) and Peters *et al.*, (1980) found an increase in THM production when pH was elevated after chlorination was terminated. Urano *et al.*, (1983) found a linear relationship between the THM formation and pH.

2.2.3.2. Temperature

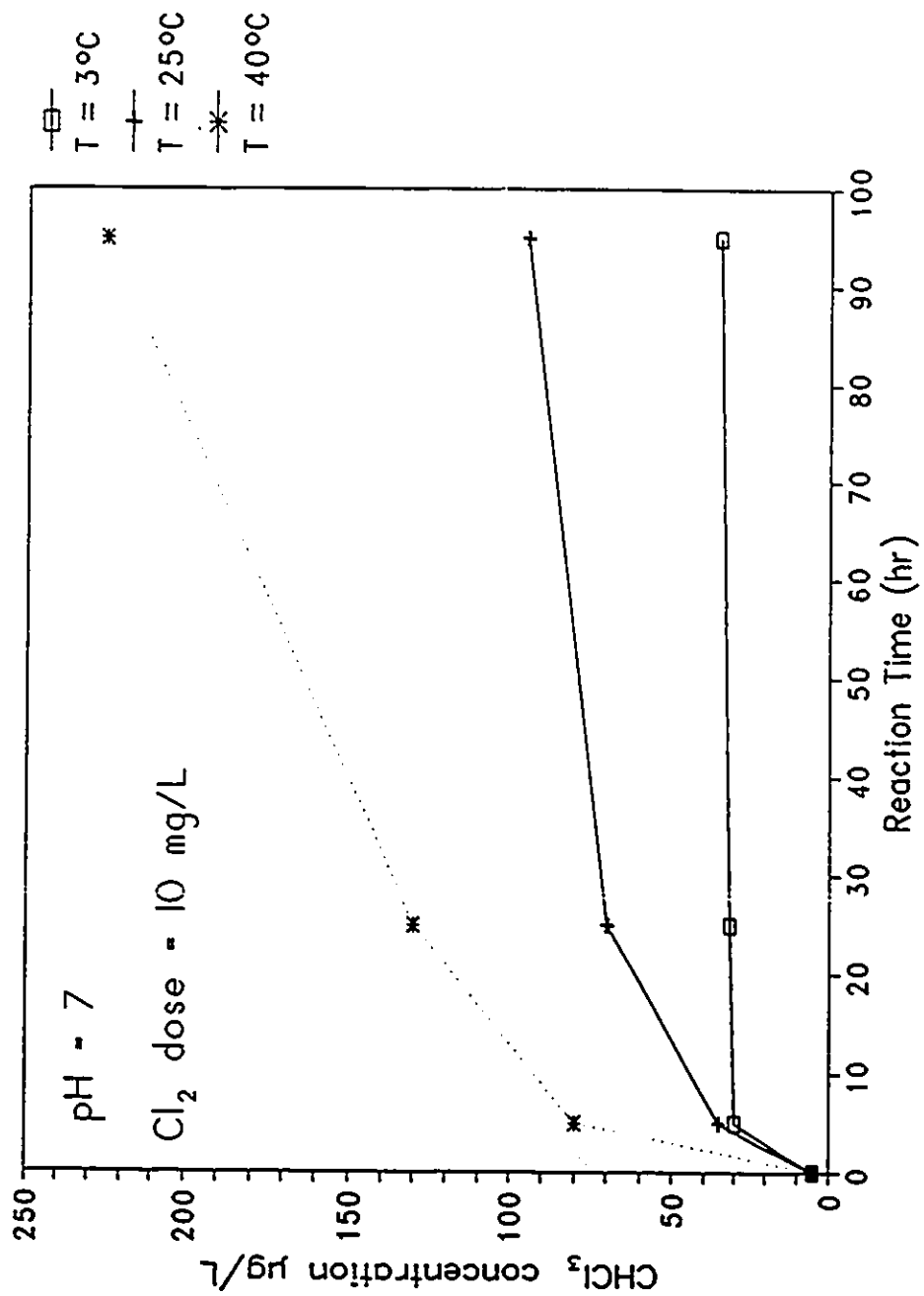
Trihalomethane formation has been found to be strongly dependent on temperature. High temperature results in high THM yield. Figure 2.6 illustrates the effect of temperature on the formation of chloroform (Stevens *et al.*, 1976). Temperature has been suggested by many researchers as one of the causes of the significant differences observed in THM values between summer and winter (Stevens *et al.*, 1976; Schnoor *et al.*, 1979; Oliver and Visser, 1980 and Uchiyama *et al.*, 1986). The increase in THM formation per 10°C rise in temperature has been estimated to be about 35-50% (Engerholm and Amy, 1983).

Figure 2.6 also illustrates that THM values are time dependent. It takes several days of reaction time between chlorine and precursors before THM reach the ultimate value.

2.2.3.3. Chlorine Demand

The relationship between chlorine dose and THM formation is complicated. THM production has been found to increase with an increased chlorine dose (Stevens *et al.*, 1976; Symons *et al.*, 1993). Other researchers, however, have shown that once a residual of several mg/L is maintained, the chlorine dose becomes far less important than pH (Oliver and Lawrence 1979; Dore *et al.*, 1982).

Trussel and Umphres (1978) have pointed out that THM formation is first a function of chlorine demand in the system for substances other than the THM precursor



Source: Stevens *et al.*, 1976

Figure 2.6. Temperature effect in chloroform production.

material. Inorganic demand is usually very rapid and exerted before appreciable THM formation occurs. They indicate that there are then two THM formation phases that occur as a function of the organic demand: a short term residual characterized by substantial linear increases in THM formation when the organic demand is high and then a long term residual characterized by modest increases in THM formation when most of organic demand has been satisfied. Engerholm and Amy (1983) found that a plateau in THM production was attained when the chlorine to TOC ratio of humic acid exceeded 5. At higher chlorine doses, only very modest increases of THM formation were observed. Urano *et al.*, (1983) found a linear relationship between THM formation and initial chlorine dose.

2.2.3.4. Bromide Ions

Aqueous chlorine is capable of oxidizing low levels of bromide ions present in natural waters to hypobromous acid (HOBr). The resulting HOBr is then available for initiating bromine addition and substitution reactions which are often faster than their analogous chlorinating reactions. As a result, numerous researchers have found that high bromide levels shift the THM speciation towards bromoform as well as increase in the total yield of THM (Cooper *et al.*, 1985). Luong *et al.*, (1982) also found that chlorine acts preferentially as an oxidant while bromine acts as a substituting agent. They have also indicated that at low *non-volatile total organic carbon* concentrations (NVTOC), the bromine substitution reaction is limiting while at high NVTOC concentrations, many reactive sites are available for both bromine and chlorine substitution. Therefore,

increasing the NVTOC concentration for a given bromide ion concentration and chlorine dose would shift the balance toward more highly chlorinated THMs.

2.2.3.5. Reaction Time

Reaction time is another important determinant of THM yield under both natural and test conditions (Rook, 1977). THMs form rapidly in the initial states of formation (up to eight hours) and more slowly thereafter but may continue to form beyond 168 hours if precursors and chlorine or bromine are present (Edzwald, 1987). The change in chloroform concentration with reaction time is illustrated in Figure 2.6.

2.2.3.6. THM Precursors

The most significant factor of THM formation is the precursor itself, the constituent that causes THM formation when reacted with either chlorine or bromine. Both the type and concentration of precursor material are important considerations (Stevens and Symons, 1977; Rook *et al.*, 1982). As described in the previous sections, humic substances are considered to be the main precursors in THM formation. Because an exact structure cannot be written for humic substances, these substances cannot be measured directly. Consequently, they are normally characterized by non-specific parameters, such as based on their ability to absorb UV light, i.e., UVA at 254 nm, by their organic carbon composition, i.e., DOC, or by their potential to form trihalomethanes (Aiken *et al.*, 1985). One of the important characteristics of humic substances that has been related to the formation of THM by many researchers is the AMSD.

2.2.3.6.1. Molecular Size Distribution of THM Precursors

The molecular size distribution of THM precursors has been studied to obtain a better understanding of the nature and sources of THM precursors and to develop suitable methods for their removal. The THM formation and yield have been reported by many researchers to be a function of precursor molecular size (Schnoor *et al.*, 1979; Oliver and Visser, 1980; Reckhow *et al.*, 1990; Amy *et al.*, 1992).

The GPC and the UF were the first methods employed in the determination of the apparent molecular mass of *dissolved organic matter* (DOM) and humic substances concentrated from water (Veenstra and Schnoor, 1980; Oliver and Visser, 1980; Collins *et al.*, 1985; Amy *et al.*, 1992). However, both techniques have been questioned in their applications because of the lack of adequate standards for their calibration, adsorption problems, present in both of them, sensitivity to different pH for GPC and non-uniformities in the pore size for UF membranes (Thurman *et al.*, 1982; Aiken *et al.*, 1985; Malcolm, 1985). The above-mentioned reasons induced other researchers to use both techniques at the same time (Collins *et al.*, 1985; Amy *et al.*, 1987; Amy *et al.*, 1988). They arrived at the following conclusions:

- ▶ Both methods provided an indication of apparent molecular mass and were capable of capturing relative changes in molecular mass distributions.
- ▶ They represent a potential analytical tool for monitoring the presence of aquatic organic matter in raw water sources as well as the removal of organic constituents in the water treatment processes.

- ▶ Generally the numerical values obtained by GPC are higher than those obtained by UF.
- ▶ Because of the operational nature of GPC and UF, caution must be used in interpreting AMS results. The relative differences as opposed to absolute values must be emphasized.
- ▶ For comparative purposes, it is important to maintain the same experimental conditions in analyzing different water sources by either of the two methodologies.

The X-ray scattering technique was used by Thurman *et al.*, (1982). This technology appears to be the most accurate method of molecular size determination to date, but the high cost of the necessary equipment to conduct this type of analysis impedes its use in most cases. High pressure size exclusion chromatography (HPSEC), due to its high resolution, efficiency and speed of analysis, has also been considered to be a potential tool for the determination of molecular size (Gloor *et al.*, 1981; Becher *et al.*, 1985).

There are conflicting reports in the literature and little or no agreement on the yield of THMFP based on the different molecular size fractions. This can be due to the lack of a standard method to concentrate and fractionate the DOM and also due to the different conditions under which chlorination was carried out.

Babcock and Singer (1979) reported that humic acids produced higher concentrations of THM than fulvic acids. This was supported by Oliver and Thurman in 1981, and corroborated later by Reckhow *et al.*, in 1990. They studied 10 aquatic humic

and fulvic acids and found that humic acids produced higher concentrations of TOX, chloroform and haloacetic acids than their corresponding fulvic acids. However, this was contradicted by the findings of Schnoor *et al.*, (1979); Oliver and Visser (1980); Collins *et al.*, (1985) and Amy *et al.*, (1992). GPC with Sephadex G-75 was employed by Schnoor *et al.*, (1979) to separate naturally occurring organics from the Iowa River into apparent molecular mass fractions that were subsequently chlorinated and analyzed for THMs. It was found that 90% of the TOC values occurred with organics having a molecular mass of less than 5000; of these 54% had a molecular mass between 3000 and 1000 and 33% were under 1000. Compounds with a molecular mass of less than 3000 gave 75% of the THMs. Using UF, Oliver and Visser (1980) fractionated aquatic humic material into eight molecular mass ranges. Each fraction was chlorinated under conditions designed to optimize chloroform production. It was found that the most important fraction for formation of chloroform (72-80%) from fulvic acids was in the range of 1,000-10,000. Collins *et al.*, (1985) studied the performance of several types of water treatment plants in removing various molecular mass fractions of naturally occurring aquatic organic matter concentrated by UF and fractionated by GPC and UF. They observed that THM reactivity ($\mu\text{g THM/mg C}$) increased with an increase in molecular mass, although the less than 10,000 molecular mass range was found to be the most consistently reactive fraction of aquatic organic matter. None of the plants was shown to be effective in removing precursor material in the less than 500 molecular mass range, although this fraction did characteristically show significant THMFP. The overall removal of THM precursors in this study was highly affected by the quality of the raw

water source.

McCreary and Snoeyink (1980), using GPC and UF, fractionated and characterized by molecular mass fractionation a commercial humic acid, a soil humic acid and extracts from leaves from a hardwood forest. They found that the THMFP per unit TOC of humic substances varied widely from source to source but was approximately the same for the different molecular mass fractions of a given source.

Amy *et al.*, (1988) used both GPC and UF to determine the AMSD for different commercial fulvic acids and for natural organic matter from the Biscayne aquifer. They concluded that the results derived from UF exhibited the same general trends as those provided by GPC. Amy *et al.*, (1990) fractionated water samples from agricultural drains by UF and found that the DOM in drain samples was characterized by a higher molecular mass. Additionally, the reactivity of the DOM with chlorine was higher than that exhibited by river and lake samples. Amy *et al.*, (1992) also characterized a ground water sample according to the AMSD expressed in terms of DOC, UV absorbance, and THMFP. It was concluded that, in general, THMFP-based distributions tended to mimic DOC and UVA-based AMSD, although in several cases, smaller AMS material was somewhat more reactive in forming THMs. They pointed out that there was no clear consensus regarding the best approach for estimated molecular mass; different methods yielded somewhat different estimates.

2.3. Control of Trihalomethanes

As mentioned earlier, there are three basic ways of controlling THMs in drinking water:

- ▶ removal of the THM precursors prior to chlorination.
- ▶ use of a disinfectant that does not generate THMs in water;
- ▶ removal of the THMs after formation;

2.3.1. Precursor Removal

Early studies done in several pilot and full scale treatment plants to evaluate the removal of THM precursors indicate that a reduction of the TOC is achieved in a conventional water treatment system (Symons *et al.*, 1975; Stevens *et al.*, 1976; Lange and Kawczynski, 1978). However, due to the raw-water characteristics, in many cases the reduction in TOC obtained by conventional treatment was not enough to achieve an acceptable level of THMs in the treated water.

The coagulation process for the removal of THM precursors has been analyzed by many researchers. Kavanaugh (1978) remarked that modified coagulation was effective in controlling the THMs and pointed out the importance of the humic substances concentration in the water source for the determination of the optimum coagulant dosage for the maximum removal of THM precursors. Babcock and Singer (1979) determined the influence of chlorination and coagulation of humic and fulvic acids and observed that coagulation of the fulvic fraction by alum results in a selective removal of those portions of the humic and fulvic acids more responsible for chloroform production. They showed

that coagulation of the humic acid fraction resulted in 86% TOC removal, compared to only 22% TOC removal from the fulvic acid fraction. Vik *et al.*, (1985) studied the effects of the coagulation process in three different water sources to determine the optimum coagulant dosage and pH for maximum removal of humic substances. They found that in all cases a pH of 5.5 was the optimum for an efficient coagulation and the water source with the greatest amount of lower molecular mass organics had the highest coagulant dosage demand and the lowest TOC removal. The maximum TOC removal varied from one water source to another (45%-81%). They attributed variation to the different chemical characteristics of the humic substances in the various water sources. Sinsabaugh *et al.*, (1986) determined the mass distribution from two Virginia reservoirs and the organic carbon removal by ferric sulphate coagulation. They found that the efficiency of coagulation was mass dependent; larger molecules (> 5000) were removed more effectively than smaller ones (< 1,000). Vick and Eikebrokk (1989) analyzed the results of several studies, on conventional and direct filtration, on the removal of humic substances. They pointed out that the main parameters affecting the coagulation of humic substances with alum include the initial concentration of humic substances in the raw water, the coagulant dosage and the pH at which the coagulation process is carried out. Kim *et al.*, (1989) studied the removal behaviour of humic substances in a conventional plant in Atlanta, GA, USA, and determined that the alum coagulation process was effective in removing high molecular mass fractions of humic substances. They concluded that the optimum coagulation conditions for both humic substances and turbidity removal were dictated by the presence of humic substances.

Adsorption by GAC has been considered to be an efficient process for the removal of THM precursors including humic substances and many other organic compounds (DiGiano, 1987; Lykins *et al.*, 1987; Zimmer *et al.*, 1989). The efficiency of this process is influenced by factors associated with the adsorbent, the adsorbate, and the aqueous system. These factors include molecular size distribution, pH, inorganic ions present, source of precursors and relative fractions of humic and fulvic acids. McCreary and Snoeyink (1980) observed that the lower molecular mass species for a given humic or fulvic acid fraction were more adsorbable than the high molecular mass species. They assumed that more surface area was probably accessible to these compounds and concluded that due to the variability in adsorption characteristics and THMFP of humic substances, adsorption results obtained at one location will likely not be those obtained at another location. Lee *et al.*, (1981) studied the adsorption of various molecular mass fractions of humic substances by selected types of activated carbon. For all carbons tested, the adsorptive capacity for the lower molecular mass fraction was determined to be greater than that for the higher molecular mass fractions. They hypothesized that size exclusion may have played a role in inhibiting larger molecules from entering smaller micropores.

Pretreatment processes like coagulation have also been reported to affect the removal of THM precursors by GAC. Lee *et al.* (1981) reported that alum coagulation enhanced both the adsorption capacity and the rate of uptake of commercial humic and fulvic acids. Weber and Jodellah (1985) corroborated these findings and pointed out that the extent of alteration in adsorption behaviours depends on the origin and type of the

humic materials involved. Chadik and Amy (1987) studied the effects of coagulation and activated carbon adsorption on the molecular mass distribution of aquatic organic matter. Alum coagulation was found to be more effective in removing higher molecular mass organic matter, while activated carbon adsorption was effective in removing organic matter in a broad molecular mass range.

Chemical oxidation, using ozone as oxidant, has also been considered an attractive alternative that can provide additional benefits to the THM precursors' removal, such as improvement in coagulation and filtration, taste and odour control and destruction of organic chemicals during the treatment of drinking water (Rook, 1976; Glaze, 1987; Amy *et al.*, 1988, Singer and Chang, 1989). In a study to evaluate the impact of ozone in the removal of TOC and THM precursors by conventional water treatment, Singer and Chang (1989) observed that preozonation alone can lower THMFP by about 10 to 15 percent at the ozone dosages commonly used in water treatment practice (0.5 - 5 mg/L). Amy *et al.*, (1988) studied the effects of ozonation on the AMSD of organic carbon and THMFP. Ozonation resulted in a significant disappearance of higher apparent molecular mass material with a corresponding increase in lower apparent molecular mass material. Little overall reduction in DOC concentrations but significant overall reductions in UVA were observed.

Argaman *et al.*, (1984) investigated different processes of a surface water treatment system, in bench scale and pilot plant with coagulation, followed by GAC and ozonation. They found that the coagulation system consistently reduced the bulk of turbidity, colour and organics in the water. GAC treatment reduced the colour and

THMFP to very low levels. Ozonation was very effective for colour removal, but little or no removal of THM precursors was obtained.

2.3.2. Use of Alternate Disinfectants

Selection of an optimum or ideal disinfectant is a difficult task because several criteria must be met:

- ▶ easy generation and widespread use;
- ▶ a good biocide with an easy to measure residual;
- ▶ fewer undesirable by-products compared to chlorine;
- ▶ cost-effective.

The more common alternatives that have been studied and come close to meeting these criteria are ozone, chloramines and chlorine dioxide.

Ozone is widely used for water disinfection in Europe and in some water treatment plants in Canada (Bablon *et al.*, 1991). In most cases, ozone has been used either for disinfection or removal of taste and odours, algae, colour and some organics. Ozone is an efficient disinfectant that does not form THMs. Upon contact with organic material, it can also reduce THM precursors, although this depends on the raw-water characteristics. Therefore, before considering ozone as an alternative disinfectant to chlorine, it is necessary to evaluate how ozone would affect THM precursor removal and other water quality aspects. The disadvantages of ozone are its higher cost compared to chlorine, its limited residual protection and its potential to form organic by-products with unknown health risks (Katz, 1980; Bablon *et al.*, 1991). In addition, ozone must be

generated on-site.

Chloramines (monochloramine) do not react with organic precursors to produce THMs (Cooper *et al.*, 1985; Cameron *et al.*, 1989). However, they are considered to be a weak disinfectant compared to chlorine. Increasing the dose and contact time may compensate for their inferior disinfection capacity. The data indicate that the effective concentration of chloramines must be 25 times that of chlorine and the exposure period required is 100 times more than that for free chlorine (Cooper *et al.*, 1985).

Chlorine dioxide is also an effective disinfectant that does not produce THMs; however, its usage must be carefully controlled because chlorine dioxide breaks down to chlorite, chlorate and chloride ions. Chlorite ions have negative potential health effects (Valenta, 1986). Other disadvantages are its higher cost compared with chlorine and it must be generated on-site. Also, there is a consensus that this oxidant can react with organics to yield other chlorinated products and it has a potential for formation of hazardous by-products (Cooper *et al.*, 1985).

2.3.3. Removal of THMs

Aeration has been reported to be an effective method for removing THMs once they are formed (Rook, 1980; Roberts and Levy, 1985), but aeration does not remove the non-volatile humic substances. If a chlorine residual is maintained and precursors remain in solution, the formation of halogenated compounds will continue in the distribution system after the aeration process. Adsorption has been used to remove THMs, but the capacity of the activated carbons for THM removal is low and rapid

breakthrough on granular activated carbon columns has been experienced (DiGiano, 1987; Lykins *et al.*, 1988; Munz *et al.*, 1990).

2.4. Summary

Humic substances are important precursors for the formation of THMs upon chlorination. However, it is not well established in the literature which fraction of the molecular size of the dissolved organic matter has more impact on the formation of THMs. The effect of the water-source characteristics, like DOC and the concentration of humic substances, are important parameters in the reduction efficiency of THMs by processes like coagulation, GAC and ozonation. The literature shows that processes like coagulation and adsorption by GAC are selective in the removal of THM precursors, affecting only specific molecular size fractions. However, most of these studies were carried out on a bench scale or were based on the results of a single sample from conventional treatment plants. Therefore, a study involving full and pilot scale treatment plants, where the selective removal characteristics of various treatment processes are analyzed, is needed.

Chapter III

METHODOLOGY

The research presented in this dissertation examined the removal of THM precursors, primarily humic substances, in water treated by a conventional process in a full scale operating plant, the *Windsor Water Treatment Plant* (WWTP). Humic substances from the Detroit River and from the treated water were isolated and characterized and their AMSD was determined through GPC.

A separate in-house pilot plant is also being operated by the *Windsor Utilities Commission* (WUC). This pilot plant is equipped with two trains: *i*) prechlorination followed by conventional treatment with GAC, *ii*) conventional treatment with ozonation before filtration followed by GAC. One set of samples from both trains was used to compare the removal of humic substances and the effects of the processes on the AMSD and the THMFP.

3.1. Windsor Water Treatment Plant

The location of the WWTP is shown in Figure 3.1. This conventional plant employs prechlorination, coagulation-sedimentation, filtration and postchlorination as shown in Figure 3.2. It has been designed for an average of flow 182,800 m³/day and in 1992, the actual average flow was 159,000 m³/day.

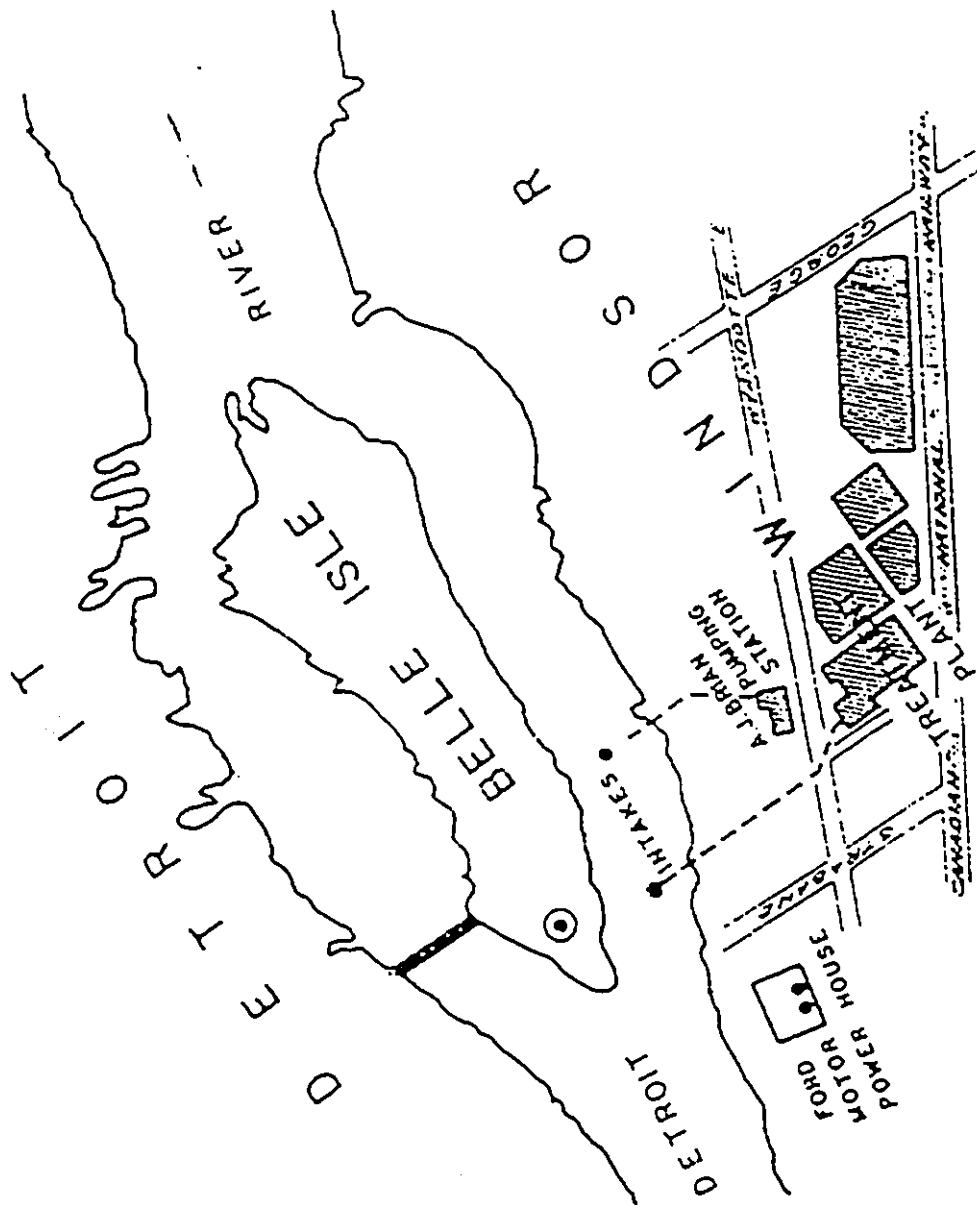


Figure 3.1. Location of Windsor Water Treatment Plant.

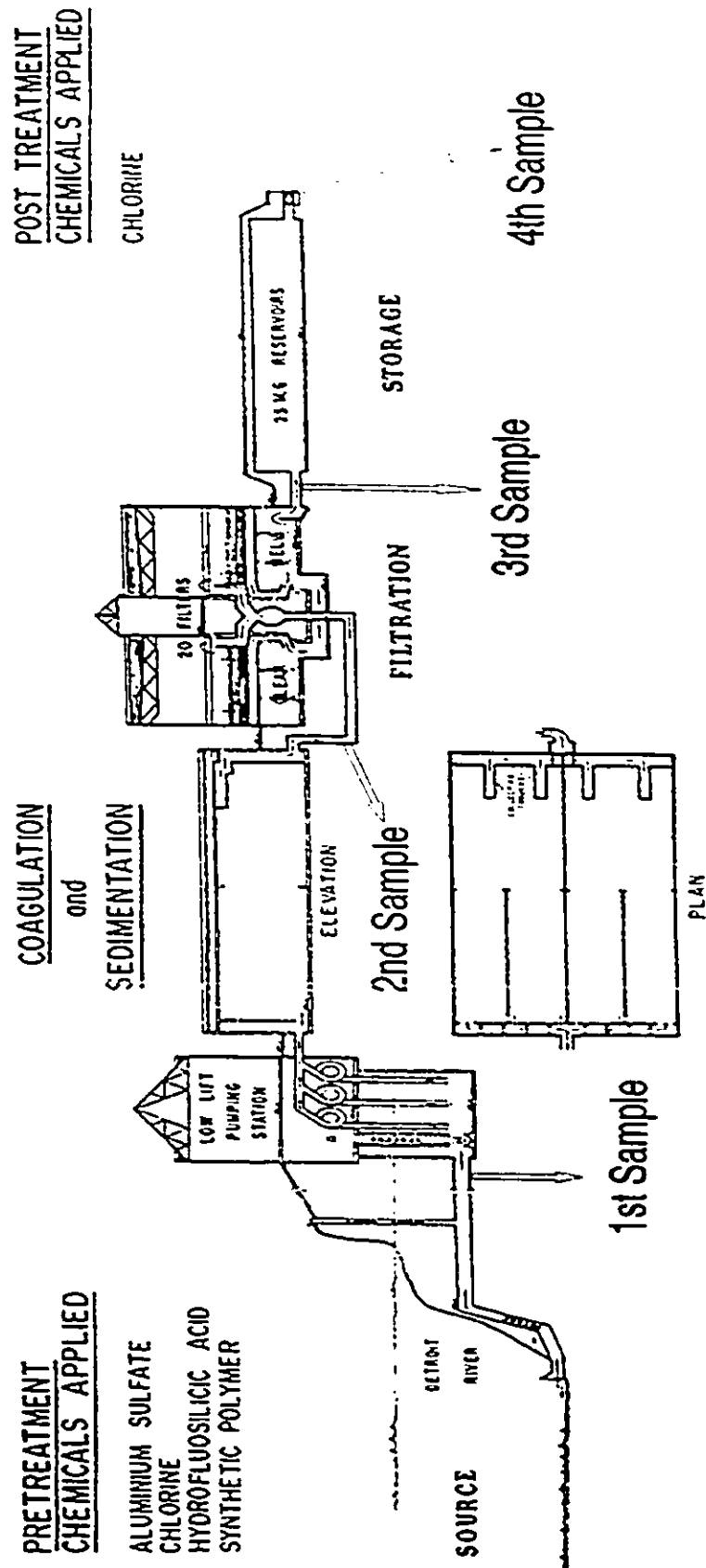


Figure 3.2. Conventional treatment at the Windsor Water Treatment Plant, and location of sampling points.

The characteristics of the raw and filtered water are shown in Table 3.1. Alum and polyelectrolytes are used as coagulant and coagulant aids in the coagulation-flocculation process. Prechlorination is normally carried out both in plant-intake and in rapid mix units, but during the summer prechlorination is changed from plant intake to the end of the sedimentation units. Also, during the summer, *powdered activated carbon* (PAC) is added to reduce taste and odour problems. The clarified water from the sedimentation basins is filtered through a dual-media (anthracite and sand) filter bed. This is followed by postchlorination.

3.2. Pilot Plant

The pilot plant is located inside the WWTP and is operated and sponsored by the MOEE and the *Windsor Utilities Commission* (WUC). It commenced operation in January, 1993 and is a part of the Environmental Technology Program initiated to stimulate the development of new environmental technologies in Ontario. The pilot plant is equipped with two treatment trains as shown in Figure 3.3.

3.3. Scope

In order to identify the AMSD and seasonal variation of the humic substances, samples of raw water at the intake of the WWTP were collected and analyzed once a month between July, 1991 and August, 1992. These samples were characterized for

Table 3.1. Characteristics of raw and filtered water at WWTP (1992).

			Raw		Filtered	
			High (mg/L)	Low (mg/L)	high (mg/L)	Low (mg/L)
Chemical Analysis	Aluminium	Al	1.17	0.26	0.21	0.06
	Ammonium	NH ₃	0.02	< 0.01	< 0.01	< 0.01
	Calcium	Ca	33.3	22	32.6	25.6
	Cadmium	Cd	< 0.0001	< 0.001	< 0.001	< 0.001
	Carbon Dioxide	CO ₂	2	0	11	4
	Chloride	Cl	14.3	9.1	13.5	10.2
	Chromium	Cr ₆	< 0.001	< 0.001	< 0.001	< 0.001
	Dissolved Oxygen	D.O.	14	8.2	13.8	8.4
	Copper	Cu	0.02	0	< 0.003	< 0.001
	Fluoride	F	0.16	0.04	1.21	0.59
	Iron	Fe	0.52	0.03	0.07	0.01
	Lead	Pb	0	< 0.001	0	< 0.001
	Magnesium	Mg	7.3	5.4	7.2	5.4
	Nitrate	NO ₃	0.91	0.51	0.86	0.36
	Phosphorous	P	0.02	0.01	0.01	< 0.002
	Potassium	K	2.1	1.2	2.1	1.1
	Silicon	Si	0.73	0.32	0.92	0.44
	Sodium	Na	7.1	5.6	6.9	5.6
	Sulphate	SO ₄	23.5	19.4	26	20.8
	Zinc	Zn	0.06	0.01	0.01	< 0.001
Solids (mg/L)						
Suspended			34.4	2.3	0.6	0.2
Dissolved			190	136	187.6	132
Total			220	138.3	188	132.5
Alkalinity (as mg/L Calcium Carbonate)						
Hydroxide			nil	nil	nil	nil
Carbonate			nil	nil	nil	nil
Bicarbonate			98.1	81.2	88.8	70.7
Total			98.1	81.2	88.8	70.7
Hardness (as mg/L Calcium Carbonate)						
Hydroxide			nil	nil	nil	nil
Carbonate			98.1	81.2	88.8	70.7
Non-Carbonate			21.1	7.1	33.9	16
Total			122	96	119	100
Physical Examination						
Colour			4	< 1	2	< 1
Taste/Odour			—	—	—	—
Turbidity NTU			74	3.2	0.95	0.3
Temperature °C			25	1	24	2
pH			8.3	8	7.6	7.1

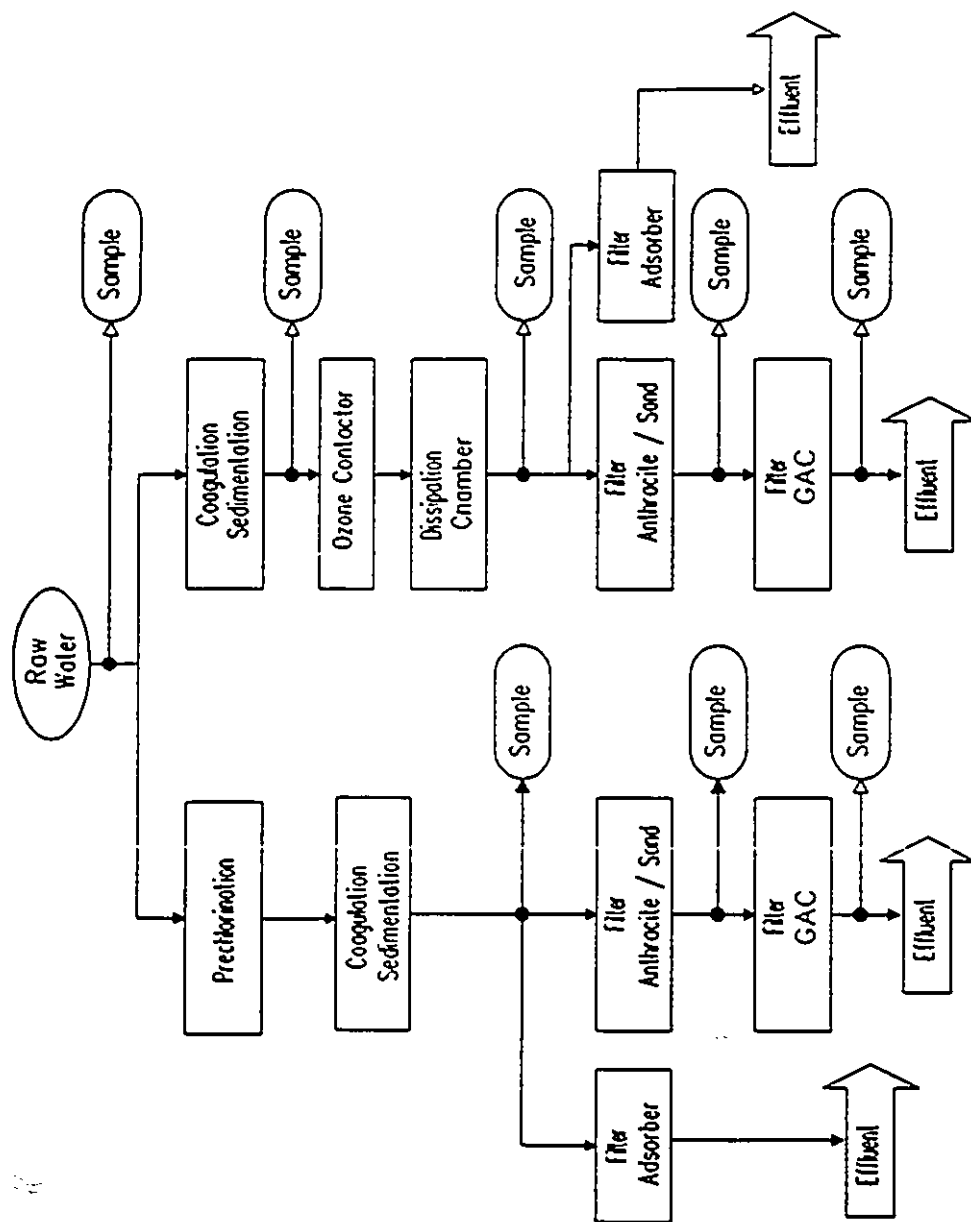


Figure 3.3. Water treatment pilot plant and sampling points (WVTP, MOEE).

DOC, turbidity, pH and AMSD. The general scheme used to characterize the samples is shown in Figure 3.4 and the various methods used are described in Chapter IV.

Samples after coagulation-sedimentation, filtration and chlorination processes were collected at the same time as the raw water to determine the removal efficiency of humic substances by the different processes (Figure 3.4). In order to detect the molecular size range of humic substances removed by each process, the humic substances were concentrated and the AMSD was determined.

The levels of THMFP in samples collected from the full scale plant were determined for the samples taken during the months of March and April, 1993. The concentrated humic substances were fractionated into three different apparent molecular size ranges in order to determine the influence of Apparent Molecular Size range on the THMFP. The range limits were based on the repetitive peaks observed in the AMSD chromatograms obtained during the sampling period from July 1991 to August 1992. In order to determine the contribution of the non-humic substances to the THMFP, these components of the sample were also analyzed for DOC, chlorine demand and THMFP. The general scheme used in the characterization and analysis is shown in Figure 3.5

A set of eight samples was taken along the pilot scale treatment plant (Figure 3.3) to compare the removal efficiency of humic substances between conventional treatment and advanced treatment processes, such as ozonation and granular activated carbon. The samples were characterized and analyzed according to the flow chart shown in Figure 3.6.

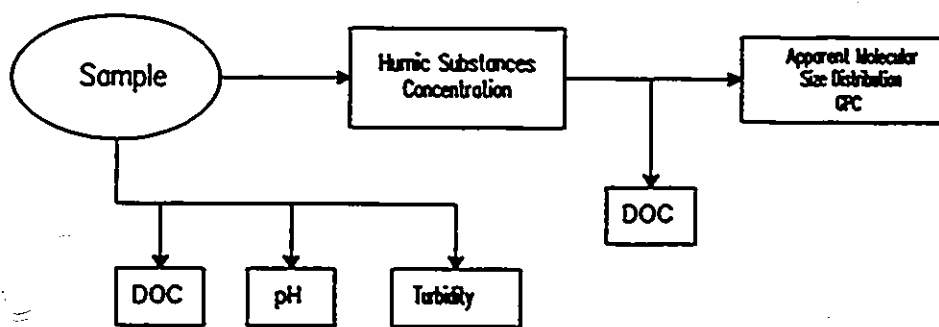
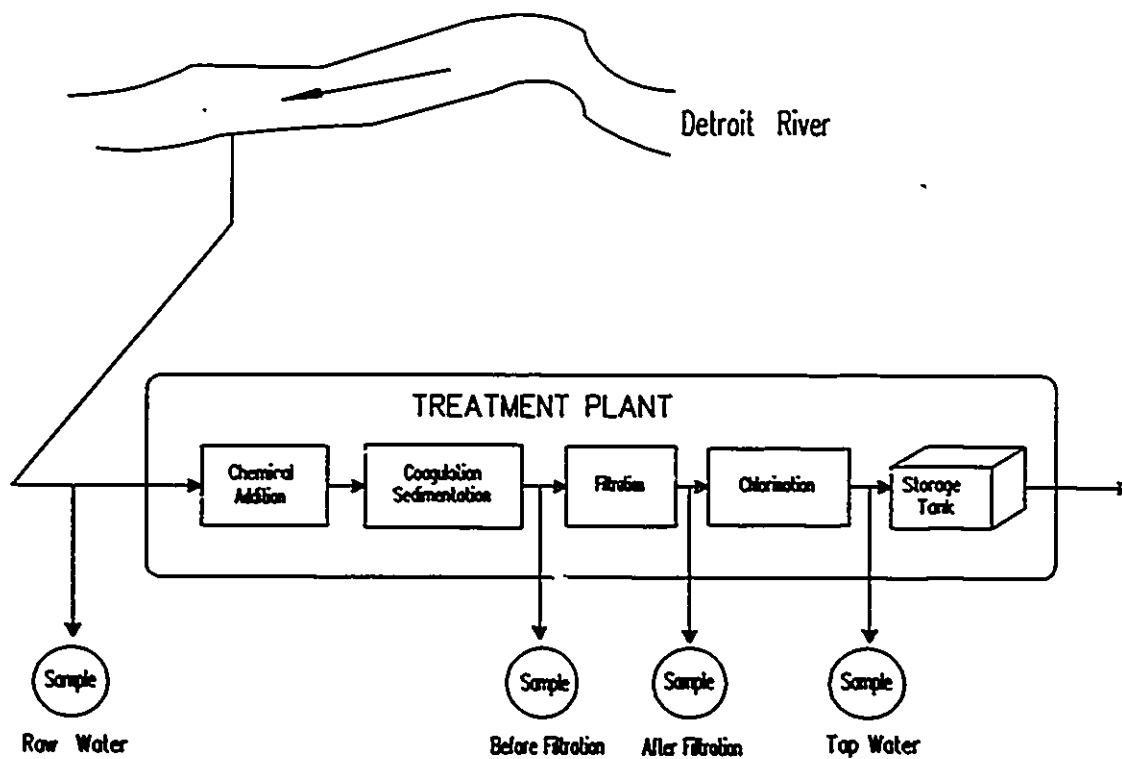


Figure 3.4. General procedure for humic substance characterization.

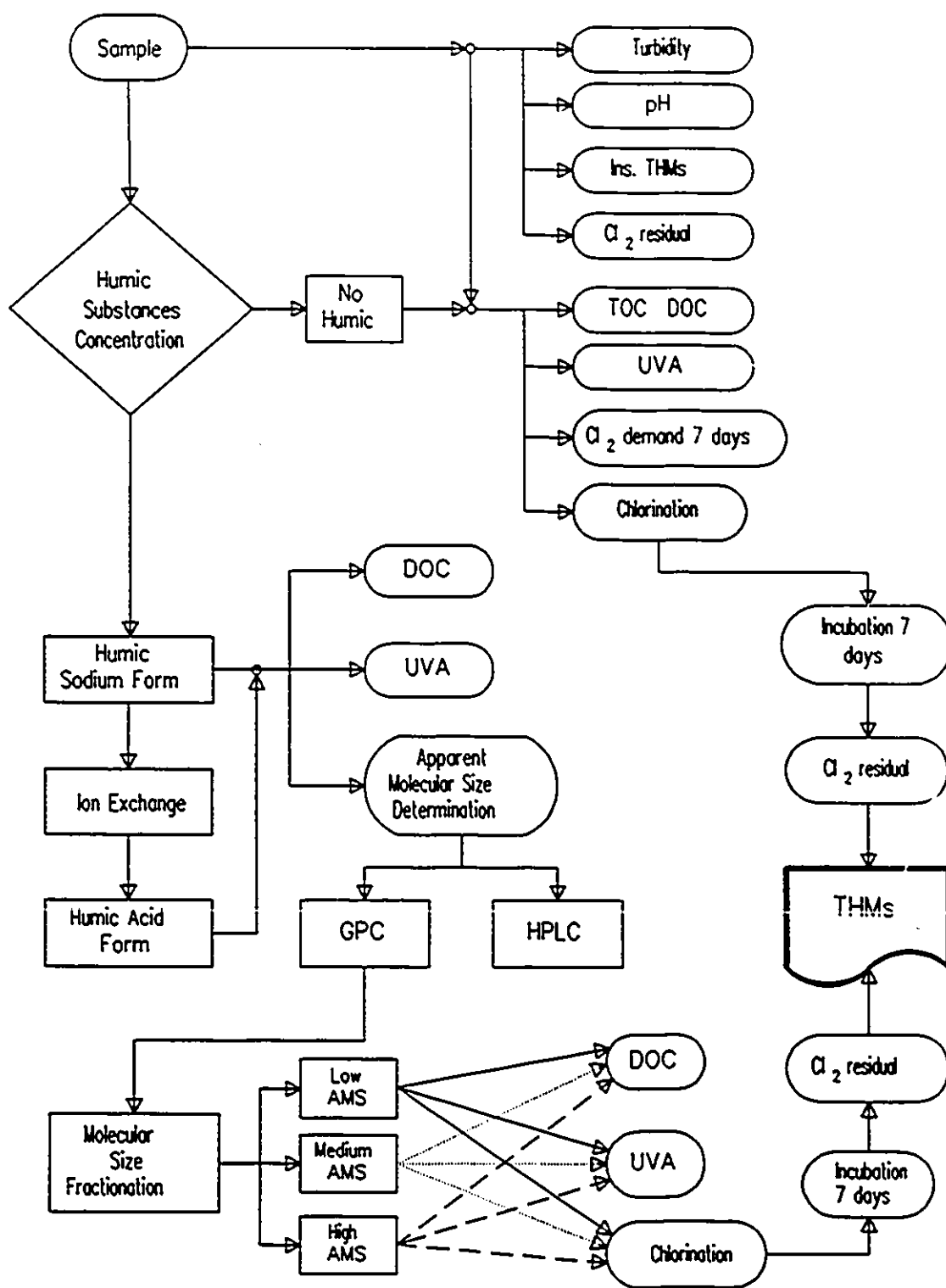


Figure 3.5. Experimental procedures flow chart for humic substance fractionation and THMFP determination.

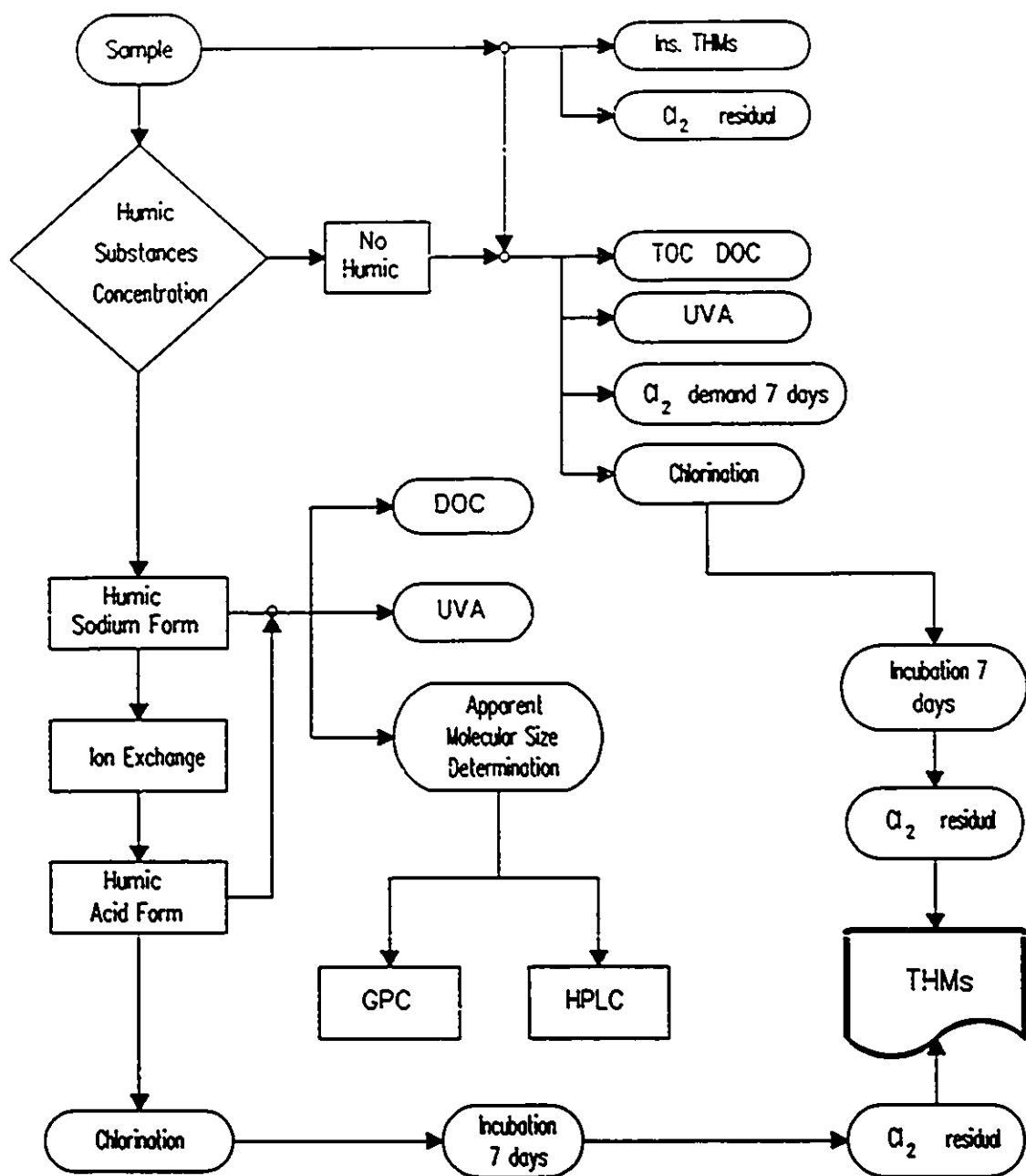


Figure 3.6. Experimental procedures flow chart for humic substance characterization in advanced treatment processes.

Chapter IV

EXPERIMENTAL PROCEDURES

4.1. General

The experimental methods employed in conducting the laboratory research which provided the data for this dissertation are described in this chapter. The methods have been subdivided into the following five categories:

- ▶ sample acquisition and storage
- ▶ sample characterization
- ▶ concentration of humic substances
- ▶ determination of AMS
- ▶ determination of THMFP

4.2. Sample Acquisition and Storage

The samples were discrete grab samples, collected in 10 L glass containers, previously cleaned with chromic acid, following Method No. 1070 in Standard Methods (APHA-AWWA-WPCF, 1989). There was no special refrigeration used in transit since the distance from the WWTP to the University of Windsor is only 5 km. The water samples were immediately analyzed for pH, turbidity, UVA, residual chlorine and instantaneous trihalomethanes. The samples were then filtered through 0.45 micron filters and kept under refrigeration at 4°C to retard biological activity.

4.3. Sample Characterization

Each sample was analyzed for the following parameters:

- ▶ pH
- ▶ turbidity
- ▶ UVA at 254 nm
- ▶ TOC, DOC.

The following section describes the equipment and analytical protocol used to evaluate each of the above characteristics.

4.3.1. pH

The pH was measured with an Orion EA 940 pH Meter using a single electrode. The pH meter was calibrated daily using standard buffer solutions. A two point calibration was used employing either a pH of 4 and 7 (for pH below 7) or 7 and 10 (for pH above 7).

4.3.2. Turbidity

Turbidity was measured with a Hach Nephelometric Turbidimeter, Model 2100A, previously calibrated and checked with reference standards before each measurement.

4.3.3. Ultraviolet Absorbance

The UVA was measured using a Hewlett Packard Diode Array Spectrophotometer Model 8452 A, equipped with a deuterium lamp as the UV source. Since UVA is a

function of pH, all samples were adjusted to pH 7 with reagent grade HCl or NaOH which were diluted to appropriate concentrations with Milli-Q Plus water. The water was generated from a Milli-Q Plus water purification system. This unit was fed with deionized water which passed through the system consisting of an activated carbon filter to remove dissolved organics, a nuclear-grade ion exchange resin to polish out inorganic ions to 18 megaohm-cm resistivity, and an organic scavenger mixture to remove trace organics to less than 10 $\mu\text{g/L}$ (Millipore, 1990).

The raw water samples and the water samples collected before-filtration were placed in a centrifuge to remove any apparent absorbance caused by turbidity. All samples were analyzed in a quartz cuvette, since glass is opaque to UV light. Milli-Q Plus water was used as the blank in all cases.

4.3.4. Organic Carbon (TOC, DOC)

The TOC and the DOC measurements were carried out with a Dohrman DC-180 Total Carbon Analyzer employing potassium persulfate as the oxidizing agent and ultraviolet light as the catalyst. The CO_2 detector was a linearized *non-dispersive infrared detector* (NDIR). The instrument was calibrated according to the procedures given in the operation manual (Dohrman, 1989), with a series of standards that encompassed the expected concentration range of organic carbon in the samples (10, 50 and 150 mg/L). The organic carbon determinations were made by injection mode, using two injections each of 250 μL . The first injection was used to determine the inorganic carbon of the sample and the second injection was used to determine the total carbon.

The organic carbon was calculated by the difference between total carbon and inorganic carbon. Blanks of Milli-Q Plus water and appropriate standards were analyzed every 5 samples to verify the stability of the instrument. The instrument precision was within 2 percent of the measured value.

The DOC samples were filtered with 0.45 micron membrane filters. All TOC and DOC samples were kept in 50 mL glass vials previously washed, rinsed and oven baked at 400°C for 4 hours in order to eliminate any possible organic contamination. When it was needed, samples were preserved with one drop of concentrated phosphoric acid and stored at 4°C until analysis, as recommended in Method 5310 C of Standard Methods (APHA-AWWA-WPCF, 1989).

4.4. Concentration of Humic Substances

The humic substances in water samples were concentrated and isolated as a hydrophobic fraction of dissolved organic matter by methyl-methacrylate resins (XAD-8) adsorption procedures (Thurman and Malcolm, 1981). A schematic flow chart of the method is presented in Figure 4.1.

4.4.1. Resin Cleaning Procedures

The resin, Amberlite XAD-8, was available from BDH Chemicals in 20-40 mesh beads. It is a macroporous methyl-methacrylate copolymer with an average surface area of 450 m²/g and an average pore diameter of 250 Å. The XAD-8 resin was prepared by

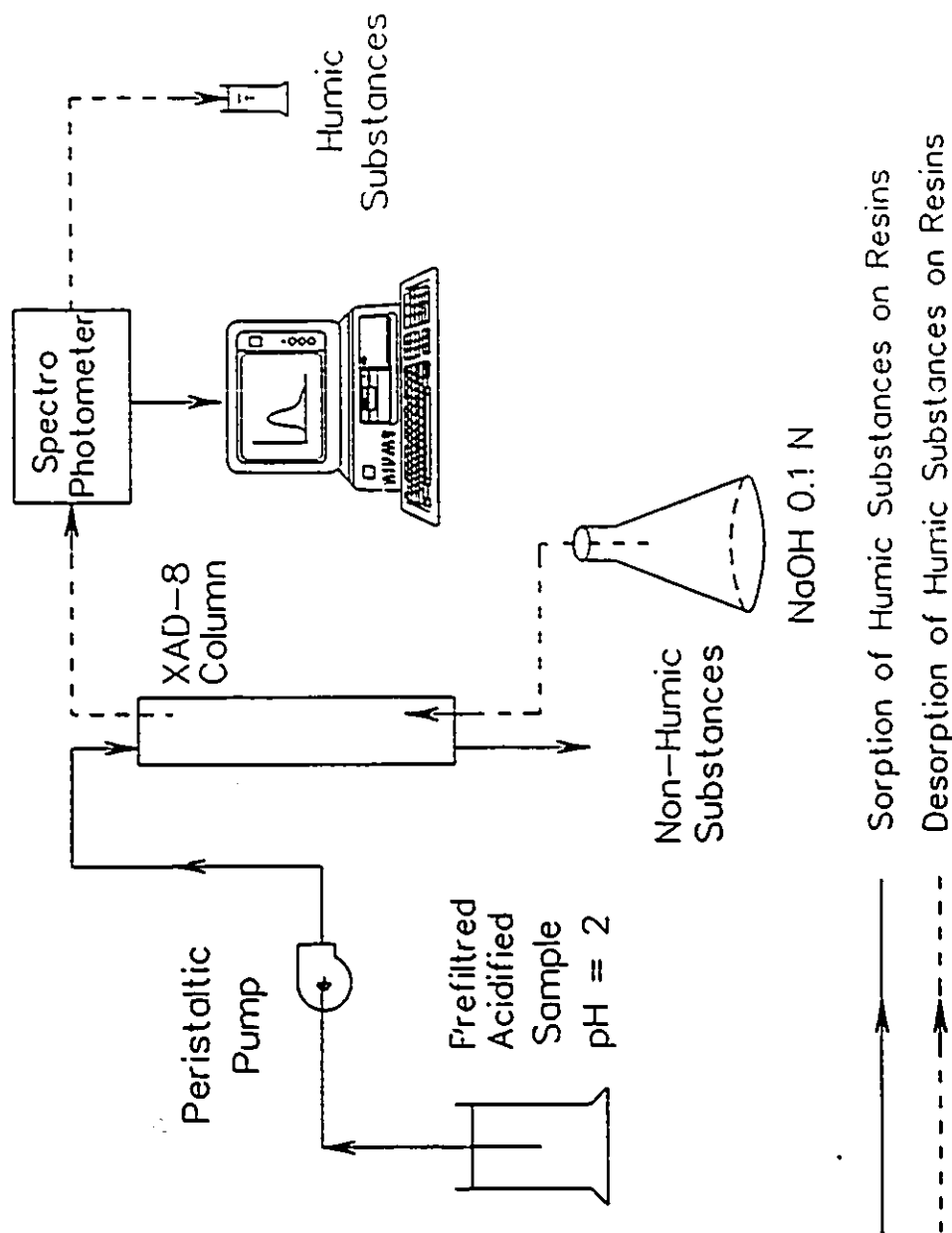


Figure 4.1. Flow chart for the concentration of humic substances.

rinsing with 0.1 N NaOH in a 2-L beaker, decanting the fines each day after successive daily rinsing of 0.1 N NaOH for five days, until the DOC of the rinse was less than 10 mg/L. After that, the resin was soxhlet-extracted sequentially with methanol, diethyl ether acetonitrile, and methanol for 24 hours each and finally stored in methanol until use (Thurman and Malcolm, 1981).

4.4.2. Determination of XAD-8 Resin Adsorbent Quantities

According to Thurman and Malcolm (1981), the size of the XAD-8 column should be chosen such that a solute with a column-capacity factor (k') of 100 is 50% retained by the column. The k' is related to column size by the following equation:

$$V_{EL} = 2 V_o (1 + k') \quad 4.1$$

where:

V_{EL} = volume of the sample that is applied to the column at 50% retention,

V_o = void volume of the column (60% of the bed volume), and

$k' = (\text{mass of solute sorbed on XAD-8}) / (\text{mass of solute dissolved in water}).$

According to Equation 4.1, an 83 mL column of XAD-8 resin was needed to concentrate the humic substances from a 10 L sample. Therefore a glass column of 15 mm diameter and 600 mm length was used to provide a total volume of 100 mL. The column fittings and tubing connections to and from the peristaltic pump were made of teflon except for the 150 mm tubing in contact with the pump roller (Masterflex pump tubing).

4.4.3. Column Preparation and Adsorption

After cleaning, the XAD-8 resin was packed in the column as a methanol/water slurry and rinsed with distilled-deionized water until it was free of methanol (less than 1 mg/L DOC). At this point, and prior to passing the sample, the column was cleaned with 0.1 N NaOH and 0.1 N HCl three times each alternating between the two solvents and leaving the column saturated with 0.1 N HCl. It is important that this rinse should precede sample application because this removes impurities that may otherwise be incorporated into the sample (Thurman and Malcolm, 1981). A fraction of the last rinse (blank rinse) was always collected for DOC determination.

Humic substances are adsorbed at an acidic pH. Therefore, all the samples were acidified with concentrated HCl to a pH of 2 and then pumped through the column at a flow rate of 10 bed volumes per hour. According to Thurman *et al.*, (1978), this flow rate gives constant values of k' .

4.4.4. Desorption

The humic substances adsorbed onto the XAD-8 resin were washed with distilled deionized water to remove excess chloride ions and then eluted in a reverse direction with 0.1 N NaOH at a flow rate of 5-bed volumes per hour. The humic substances were monitored and recaptured from the effluent by detecting the pH and the effluent UV absorbance at 254 nm.

No fulvic/humic split was made except for the sample collected in April 1993. For this sample, the analysis included the determination of the humic/fulvic relative

concentration, its AMSD and the THMFP.

4.4.5. Precision

The overall precision of this method varied from 4% to 8%. The carbon analysis of the eluate contributed 2% of the analytical error, the resins after all the cleaning procedures (resin blank showed less than 0.6 mg/L DOC concentration) contributed another 1% error and the non-humic substances that could be adsorbed in the resins added additional error from 1% to 5% during analysis of most natural waters, (Thurman, 1984).

4.4.6. Isolation

Humic substances were analyzed for AMSD as the concentrated basic form desorbed from the XAD-8 column, also called sodium humate and sodium fulvate, (Thurman and Malcolm, 1981). In addition, samples were isolated from the inorganic salts and analyzed for AMSD in the free-acid form (humic and fulvic acids). In order to obtain the free-acid form, the concentrated sodium humate and fulvate were passed through a 5 mm × 300 mm column of cation exchange resin (Dowex 50W-X8) in the form of ion hydrogen. First, the hydrogen-form resin was cleaned by soxhlet extraction with methanol for 24 h. After that, the resin was packed as a methanol-water slurry and rinsed with distilled-deionized water until free of methanol. Following this, a solution of ammonium hydroxide (NH_4OH) of 3 N strength was pumped through the column until the breakthrough was observed. Then the bed was hydrogen-saturated by pushing through

four bed volumes of 2 N strength HCl. This was followed by the rinse with distilled deionized water until the specific conductance of the effluent was less than $10\ \mu\text{S}$, (Leenheer, 1981). The sodium humate and fulvate were passed through the column and recaptured from the effluent in the free-acid form by continuous monitoring of the pH and the effluent UV absorbance at 254 nm.

4.5. Apparent Molecular Size Procedures

4.5.1. Gel Permeation Chromatography (GPC)

GPC was used to determine the AMSD of humic substances. The gel filtration system consisted of a chromatography glass column, a sample applicator, a peristaltic pump, an UVA detector and a fraction collector as shown in Figure 4.2.

4.5.1.1. Column Preparation

The glass column, (16 mm \times 400 mm) Pharmacia C-16/40, was filled with Sephadex G-75 gel (Pharmacia Fine Chemicals) which was prepared according to the manufacturer's recommendations by allowing it to swell in a buffer solution of 10^{-3} M NaHCO_3 for 24 h at 20°C . The fine particles were removed by suction and the gases were removed by applying a vacuum over the mixture for 3 hours. Then gel was then poured into the column in a single operation (Pharmacia, 1982). The eluent was a 10^{-3} M NaHCO_3 solution prepared with distilled-deionized water, degassed and filtered through a 0.45 micron membrane filter. The pH of this solution was 7 and the flow

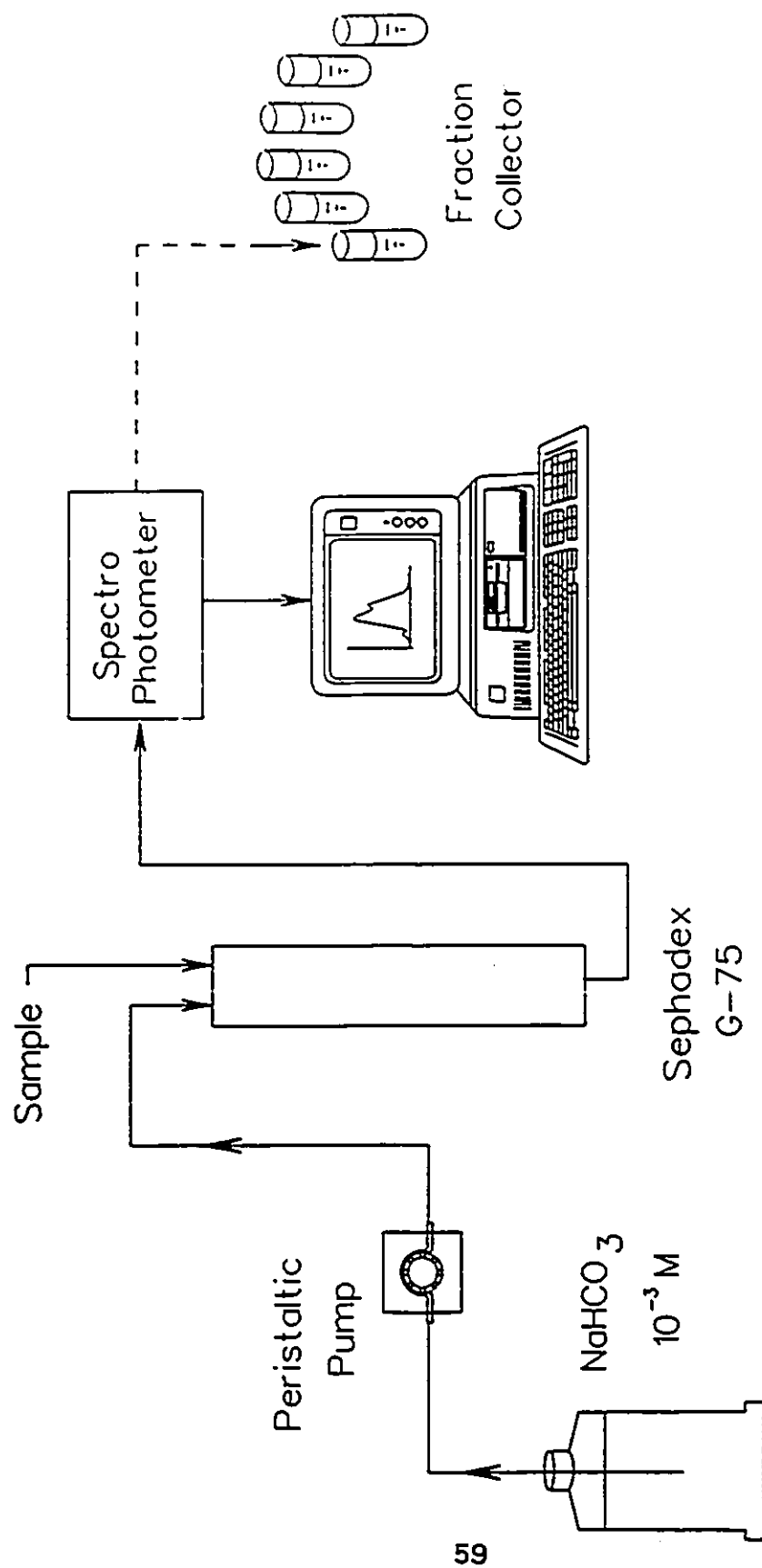


Figure 4.2. Procedure for apparent molecular size determination.

through the column was maintained at 0.15 mL per minute with a peristaltic pump.

In a typical run, 1 mL of the isolated humic substances was applied at the top of the column into a continuous flow of eluent. Organics in the effluent from the gel column were continuously monitored with a Hewlett Packard Diode Array Spectrophotometer, Model 8452 A, at 254 nm. The fractions were collected for the March 1993 and April 1993 samples and retained for DOC and THMFP analyses. The fraction collector used was a programmable Pharmacia fraction collector with 10 mL vials that had been cleaned according to the procedures outlined in the Method No. 1070, Standard Methods, (APHA-AWWA-WPCF, 1989). The collected fractions were 6.6 mL each.

4.5.1.2. Column Calibration

GPC principles indicate that there should be a linear relationship between the *elution volume* for a particular sample, V_e , and the log of the molecular size of the sample. The elution volume, V_e , was determined from the peak of a plot of the UV absorbance versus the volume collected in a GPC run. The *void volume*, V_o , was determined by using a solution of blue dextran (molecular size = 2,000,000) as a sample (Fischer, 1980). The blue dextran with such a high molecular size was unable to penetrate the gel. Blue dextran also served as a means of checking the packing of the gel since irregularities and air voids in the gel would have caused the blue colour to disperse irregularly rather than travel through the gel in a tight uniform band which indicates good operation (Pharmacia, 1982). Observations of this blue dextran run, made after the column was initially established and at various times thereafter, indicated that the column

was properly packed and was stable throughout the study.

Several proteins of various molecular sizes, as shown in Table 4.1, were used to calibrate the gel. Duplicate and in some cases triplicate runs, were used to determine the appropriate V_e values for these standards. The calibration yielded a straight line on a semi-log plot of molecular size vs. elution volume plot (Figure 4.3).

Table 4.1. Standards for GPC calibration.

Protein	Molecular Size	V_e/V_o
Albumin	67,000	1.10
Ovalbumin	43,000	1.29
Chymotrypsinogen	25,000	1.71
Ribonuclease	13,700	1.84
Cytochrome C	12,400	1.94
Vitamin B-12	3,500	2.66
Blue Dextran 2000	2,000,000	

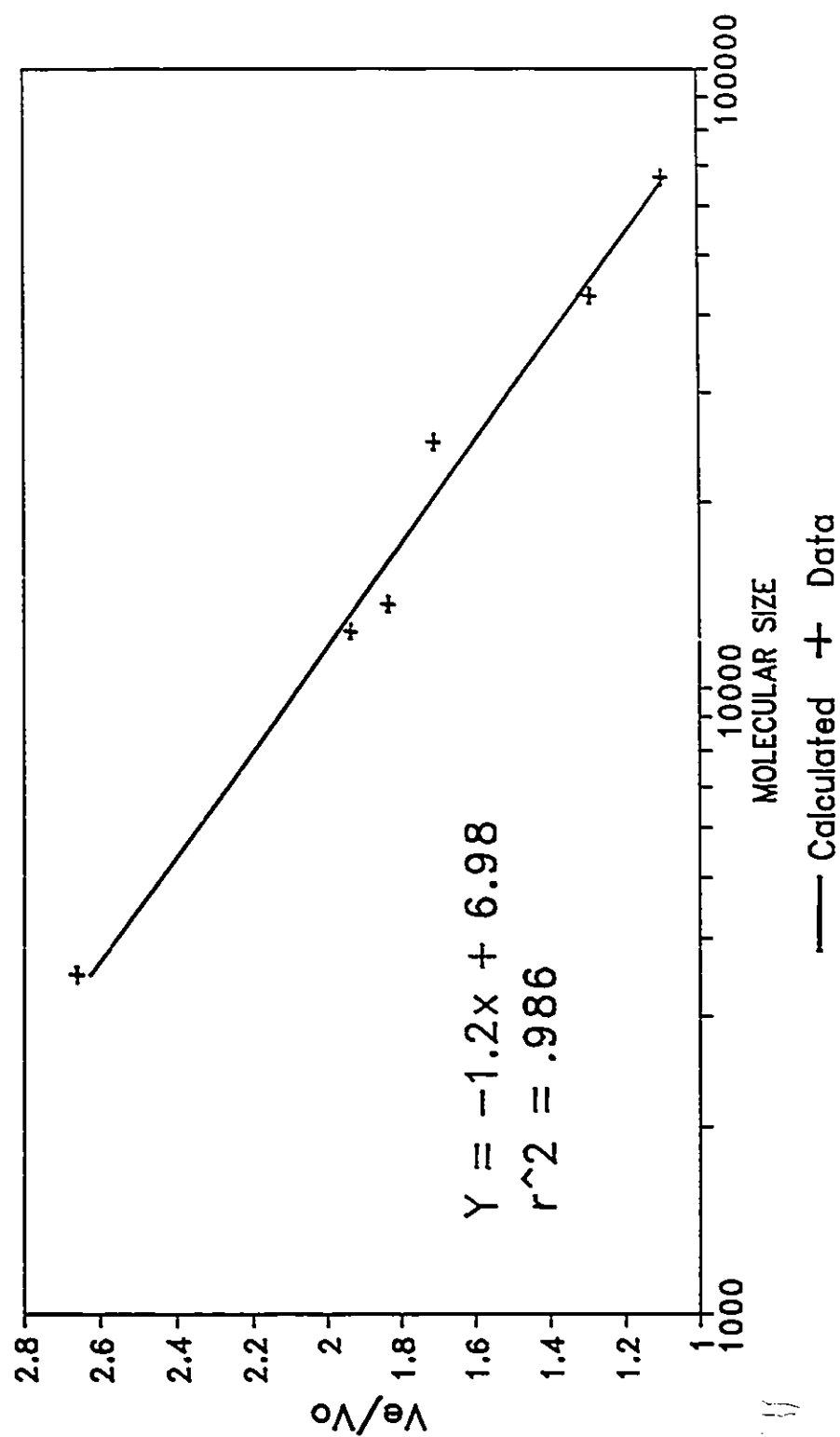


Figure 4.3. Gel permeation column calibration curve.

4.5.2. High Performance Size Exclusion Chromatography (HPSEC)

Since the determination of molecular size by gel permeation chromatography is time consuming (8 h per sample), a high pressure liquid chromatography system (HPLC) was acquired. Determination of the apparent molecular size distribution for the water samples was carried out in the new system and the run time was reduced to 40 minutes per sample.

The HPSEC was carried out at ambient temperature. The HPLC system consisted of a Waters 712 WISP Model Injector and a Waters 486 Model UV Absorbance Detector operating at 254 nm. The column used was a 7.8 mm \times 300 mm Protein Pak 125 column packed with a silica based material. The void volume was determined with Blue dextran 2000 as explained earlier. Various concentrations of the eluent solution and flow rate were tested before samples were analyzed. A 0.02 M KH_2PO_4 + 0.18 M NaCl buffer with a pH of 6.5 and a flow rate of 0.5 mL \cdot min⁻¹ gave the best resolution of the humic substances studied. Injection volume was 50 μ L. The calibration curve was obtained with the same proteins as in the GPC procedure and it was found to be linear in the selected range, as shown in Figure 4.4.

4.6. THM Formation Potential Determinations

The THMFP determinations were made according to Method No. 5710 B. in Standard Methods (APHA-AWWA-WPCF, 1989). All samples were buffered with a

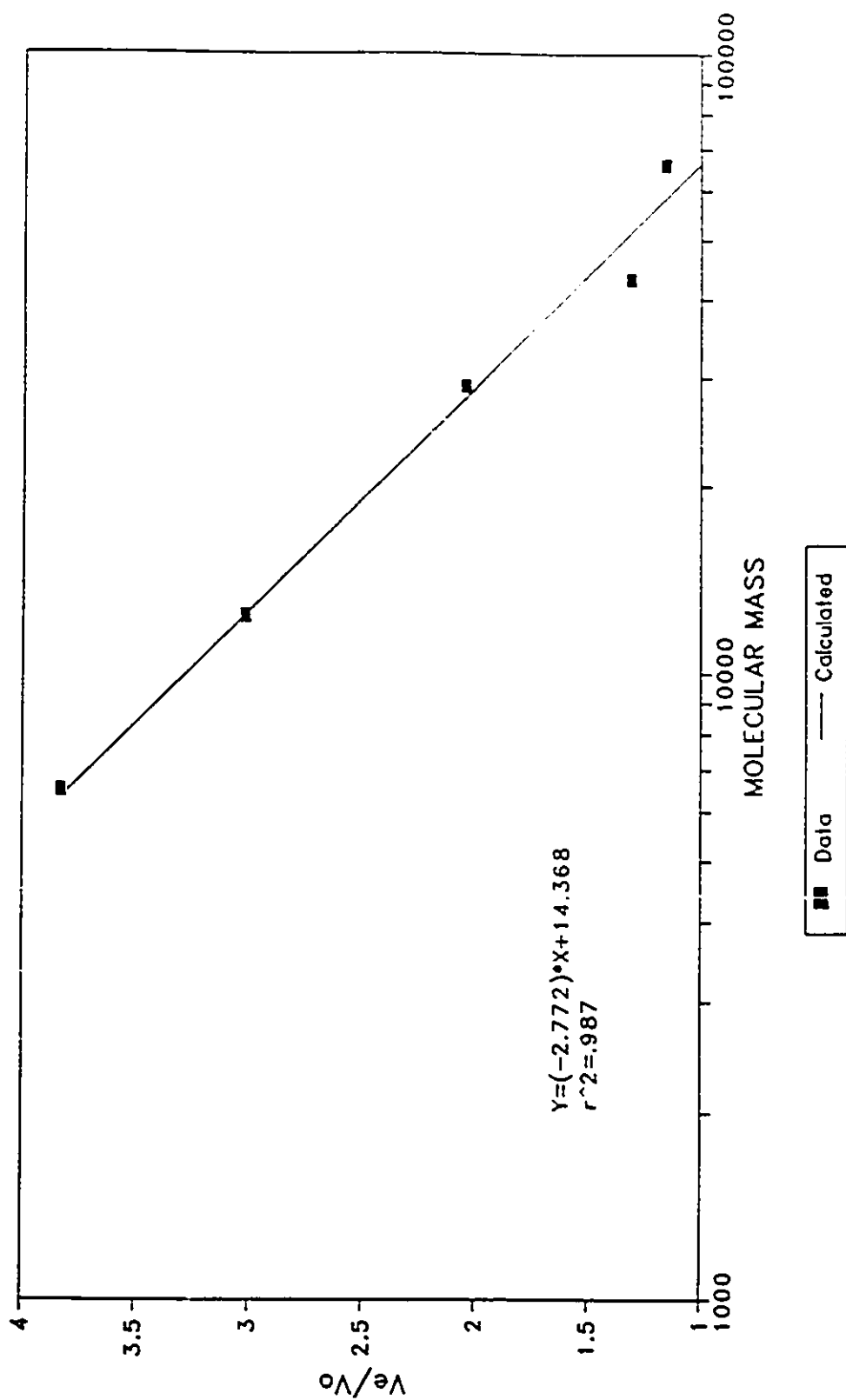


Figure 4.4. HPSE column calibration curve.

0.1 M phosphate buffer. The pH was checked with a pH meter after mixing to insure the proper pH level. The buffer capacities were checked by dosing aliquots with hypochlorite solutions and remeasuring the pH. The buffered samples were then placed into bottles (serum vials) of various sizes according to the sample volumes available. A volume of 250 mL was used for the initial and the non-humic samples and a volume of 47 mL was used for the concentrated samples of humic substances. The volume of all the fractionated samples was 12 mL.

The samples were then placed in an incubator set at 25°C and allowed to attain this temperature. These were removed from the incubator and chlorinated with stock sodium hypochlorite solution which had been standardized by the iodometric method as detailed in Method No. 4500 CL B, Standard Methods (APHA-AWWA-WPCF, 1989). After this, the vials were closed with teflon-coated septa threaded caps, checked for free headspace and returned to the incubator for 7 days. The blank reagent contained only the phosphate buffer and Milli-Q Plus water with and without chlorine. These were analyzed in all sets of samples. The chlorine dose was based on the 7-day chlorine demand for the sample that had been previously determined for the initial sample and non-humic substances.

After the incubation period, samples were taken out and analyzed for residual chlorine, according to Standard Methods, Method No. 4500-CL D (APHA-AWWA-WPCF, 1989). The chlorine reaction was quenched by adding 0.1 N sodium sulphite solution and lowering the pH to 2 with concentrated HCl. The samples were stored in the dark at 4°C until THM analysis were carried out.

4.6.1. Chlorine Demand

Chlorine demand of the samples and their corresponding non-humic fractions were determined by spiking a high chlorine dose to the sample and measuring the chlorine consumed by the sample at different periods of time. A 250 mL sample was used for this determination.

First the sample was adjusted with a phosphate buffer to a pH of 7, then the chlorine dose was added and mixed. After that, each chlorinated sample was split into five brown vials of 47 mL each, filled completely with the sample, sealed with TFE-lined screw caps and stored in the dark at 25°C. After different periods of time (1, 2, 4 and 7 days), one vial of each sample was taken out and analyzed for residual chlorine (Standard Methods, Method No. 4500-CL D (APHA-AWWA-WPCF, 1989)). Chlorine demand was calculated from the difference of the initial dose and the residual chlorine at different times.

4.6.2. THM Analysis

The THM determinations were done using an automated purge and trap system (Tekmar LSC 2000 Model 5010) to concentrate the samples prior to determination by a computerized gas chromatography/mass spectrometer system. The GC-MSD system consisted of a Hewlett Packard HP 5890A gas chromatograph and a HP-5971A *mass selective detector* (MSD), controlled by a HP G1034C MS ChemStation for data analysis. All operating conditions were programmed according to the specifications given in the USEPA Method 501.3 (1982).

4.6.2.1. Analytical Procedure

The Tekmar LSC 2000 was equipped with 16 individual injection ports with 5 mL volume glass vials. However, only 9 of them were used because only these ports were equipped with a glass frit necessary to improve the efficiency of the purging. A maximum of 6 samples was analyzed during each complete run and two positions were used for reagent water blanks, prepared according to Method 6210 B, Standard Methods (APHA-AWWA-WPCF, 1989). The blanks were run for all sets of samples to verify acceptable levels of interferences and contaminants in the system. The ninth position was used as laboratory control to verify the precision and efficiency of the system.

4.6.2.2. Calibration

The internal standard method was used to calibrate and quantify the concentrations of THMs in the samples. An internal standard is a pure compound added to a sample in known amounts and used to calibrate concentration measurements of other compounds that are sample components. A solution of 1, 4-dichlorobutane was used as internal standard and was added to all the samples (USEPA Method 501.3, 1982).

A calibration curve was prepared by analyzing 5 different concentrations of THMs prepared from a certified stock (Aldrich chemicals). Each standard solution was spiked with 10 μ L of internal standard solution. The standard solutions were analyzed using the same procedures that were used to analyze the samples.

The measurements of THMs were quantified by calculating the mass spectrometer response to each compound relative to the internal standard. The response factor (RF)

was calculated with the equipment's computer software for each compound using the basic equation:

$$RF = \frac{A_x \cdot Q_s}{A_s \cdot Q_x} \quad 4.2$$

where:

A_x = integrated abundance of the selected ion for the trihalomethane standard,

A_s = integrated abundance for the selected ion for the internal standard,

Q_s = quantity of internal standard, and

Q_x = quantity of trihalomethane standard.

Sample concentrations were calculated using the equation:

$$C_x = \frac{A_y \cdot Q_s}{A_s \cdot RF \cdot V} \quad 4.3$$

where:

C_x = analyte concentration in $\mu\text{g/L}$,

A_y = integrated ion abundance of the primary characteristic ion of the sample analyte,

A_s = integrated ion abundance of the primary characteristic ion of the internal standard,

Q_s = quantity of internal standard added in μg , and

V = purged sample volume in litres.

One or more standards were analyzed daily to verify that the response factors had not changed. When more than 10% relative standard deviation was detected, new standard solutions were prepared and analyzed to determine the new response factors. In order to determine the efficiency of the purge and trap instrument, different sets of the same concentration standards were run as samples. The efficiency was calculated to be 93% for CHCl_3 and 97% for CHCl_2Br , CHClBr_2 and CHBr_3 .

Chapter V

RESULTS AND DISCUSSION OF FULL SCALE STUDIES

This chapter presents the results of the measurements and analysis of the humic substances from the Detroit River. An evaluation of the removal efficiency of humic substances by the different treatment processes at the WWTP was carried out over a period of 16 months. In addition the different molecular size ranges as affected by the various treatment processes were also determined. A comparison between the humic substances from the Detroit River characteristics and the standard humic substances from the IHSS has also been carried out.

5.1. Humic Substances

Humic substances were isolated from the untreated and treated water samples using the Thurman-Malcolm procedures described in Chapter IV. Concentrations were determined in terms of dissolved organic carbon and expressed as mg/L of humic substances. Results presented in Table 5.1 indicate that an average of 30% of the total DOC corresponds to humic substances. The remaining DOC is due to non-humic substances. Comparing these results with the general composition of humic substances in various kinds of natural waters as presented by Thurman (1985), it is found that this is consistent with the low concentration range of humic substances in rivers and is within the range of humic substances concentration found in lakes. This is not surprising because the Detroit River is a connecting channel between Lake St. Clair and Lake Erie,

with a low water temperature due to its geographic location, hence the low average turbidity and the low average concentration of humic substances and DOC.

Table 5.1. DOC distribution in Detroit River water.

Sample	Sample DOC mg/L	Non-Humic DOC mg/L	% Humic	% Non-Humic
25-Jun-91	2.31	1.62	30	70
23-Jul-91	1.90	1.39	27	73
20-Aug-91	2.50	1.88	25	75
23-Sep-91	2.00	1.46	27	73
21-Oct-91	1.91	1.39	27	73
30-Jan-92	2.00	1.43	29	71
19-Feb-92	2.00	1.48	26	74
13-Mar-92	2.05	1.50	27	73
10-Apr-92	2.70	1.81	33	67
22-May-92	2.40	1.68	30	70
Jun-92	2.60	1.85	29	71
Jul-92	2.50	1.70	32	68
20-Aug-92	2.70	1.81	33	67
1-Mar-93	2.50	1.80	28	72
13-Apr-93	3.20	2.11	34	66
6-Oct-93	2.17	1.63	25	75
Average:	2.27	1.61	29	71

5.1.1. Seasonal Variation

A seasonal variation in the concentration of humic substances was observed during the sampling period from August 1991 to August 1992, as shown in Figure 5.1. As a general trend, the humic substances concentration remained almost constant during the winter months, increased during the spring when the turn-over in water bodies occurred, reached a maximum in April, decreased during May and June, increased again during the summer months and decreased again during the fall. Samples from March, April and October 1993 showed the same tendency (Figure 5.1).

Since the rate of formation of THMs is highly dependent on water temperature, the maximum values of THM concentrations are expected to occur during the summer months. However, THM formation depends also on the precursor concentration, which according to the results of this research, appear to be highest during the spring turn-over. Similar variations in organic contents and humic substances were found by Huck *et al.*, (1987). These researchers associated the high humic substances content with spring thaw and run-off which normally occurs with an increase in ambient temperature and at the same time causes the spring turn-over in water bodies.

Figure 5.2 shows the seasonal variations in THM concentrations in WWTP tap water, as reported by the MOEE (MOEE, 1991-1993). This trend is similar to that observed above for humic substances, some of which would combine with chlorine to form THMs. The maximum values were reported in April 1992 and in the summer months of 1991. The minimum values were obtained during the fall. These results indicate that the spring turn-over is an important environmental factor that results in

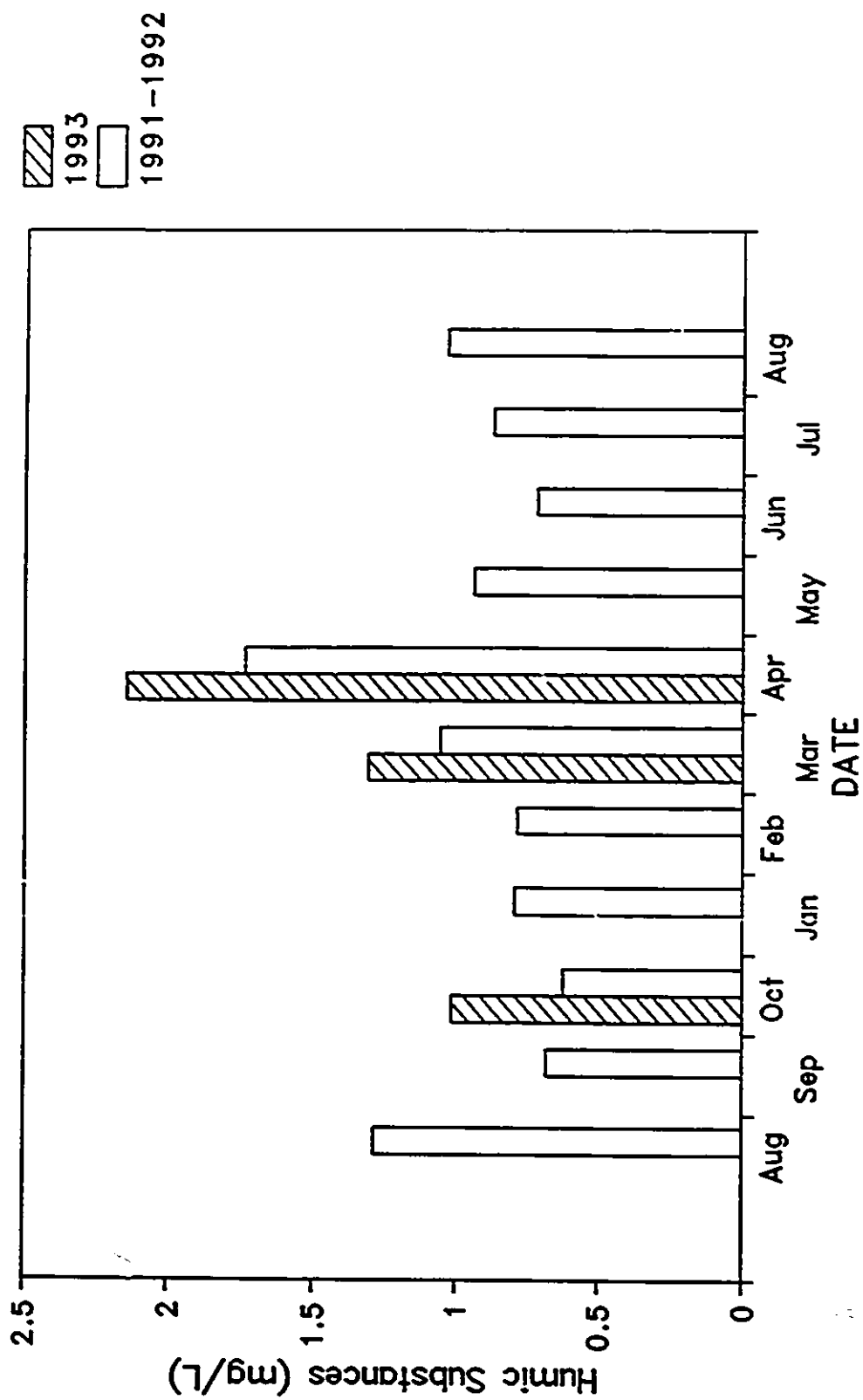
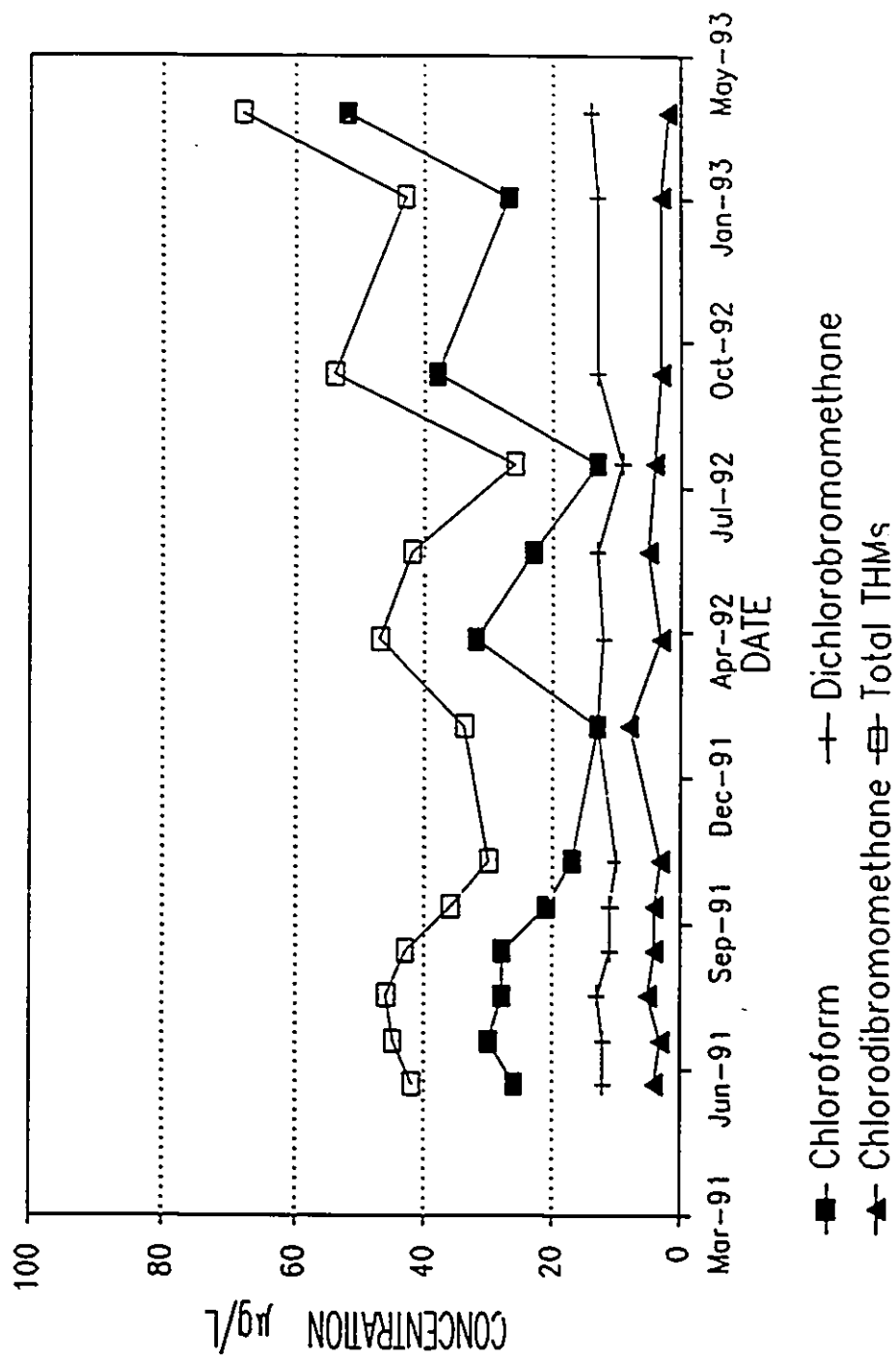


Figure 5.1. Seasonal variations of humic substance concentrations in Detroit River water.



higher levels of humic substances in water and, consequently, higher concentrations in THMFP.

The seasonal variations in humic substances also show a relationship to variations in raw-water turbidity, chlorine demand and *powder activated carbon* (PAC) dosage. These data were obtained from the WWTP and are shown in Figures 5.3 and 5.4. It can be seen that both humic substances and turbidity show similar trends, with peaks in April and low values in the fall. This suggests that some of the humic substances were either in colloidal form or had been adsorbed on suspended solids. It is further observed that the chlorine demand during prechlorination was extremely high when PAC was added. This was due to the adsorption of chlorine by PAC. After adjusting the prechlorination demand for PAC, based on data in Figure 5.4, it is observed that the chlorine demand during prechlorination is high in April when both humic substances and turbidity are high. The association of high turbidity and chlorine demand with humic substances content has also been reported by Huck *et al.*, (1987).

5.1.2. Removal of Humic Substances by Conventional Treatment Process at the WWTP

Various water treatment processes are capable of removing humic substances from natural water sources. Figure 5.5 illustrates the average removal behaviour of humic substances at the WWTP. The concentration of humic substances decreased from an average of 1.07 to 0.7 mg/L. Similarly the treatment processes decreased the concentration of DOC from an average of 2.2 to 1.8 mg/L as C. These concentration

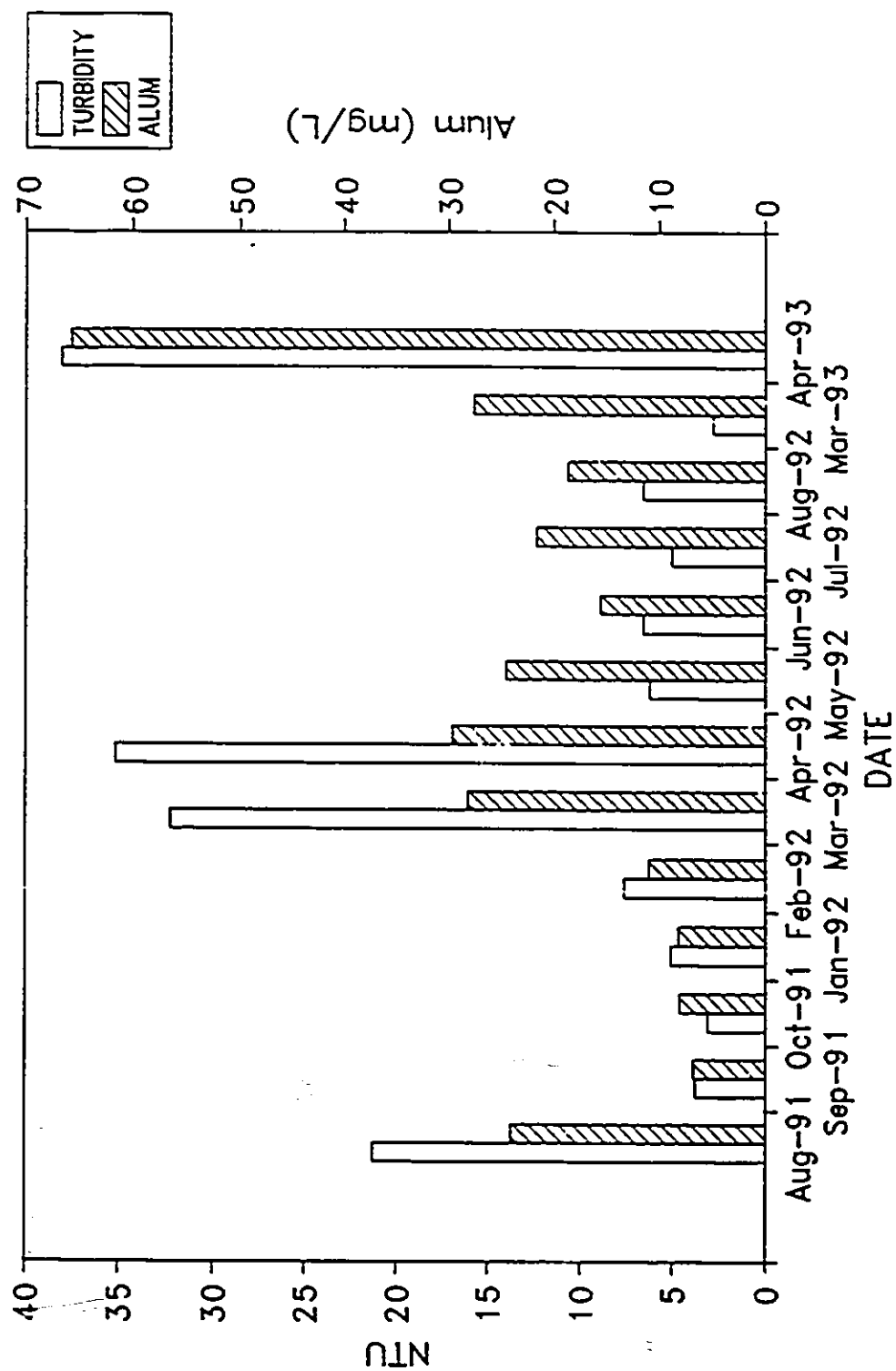


Figure 5.3. Seasonal fluctuations in turbidity and chemical dosage at the WWTP .

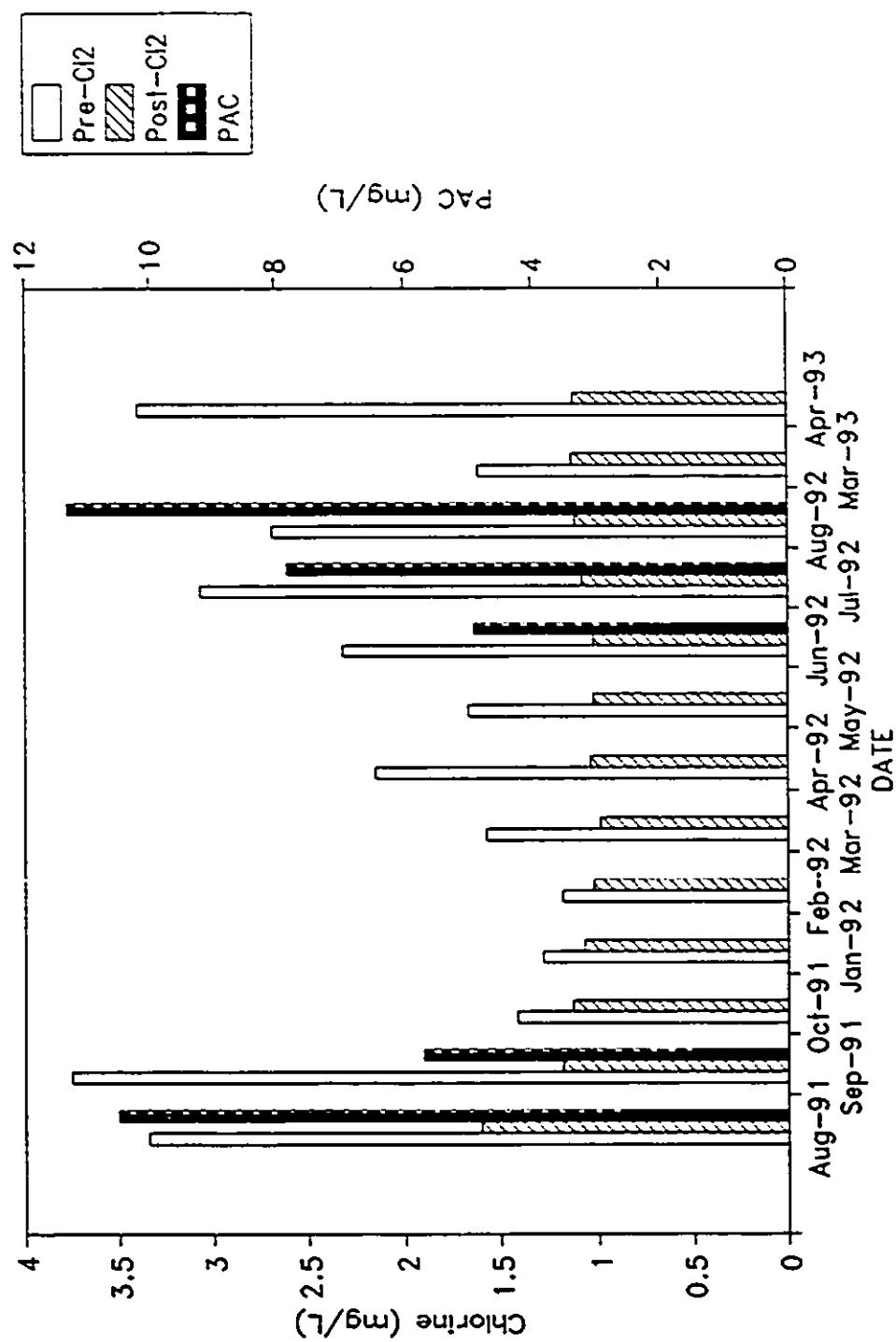


Figure 5.4. Seasonal fluctuations in chlorine demand and chemical dosage at the WWTP.

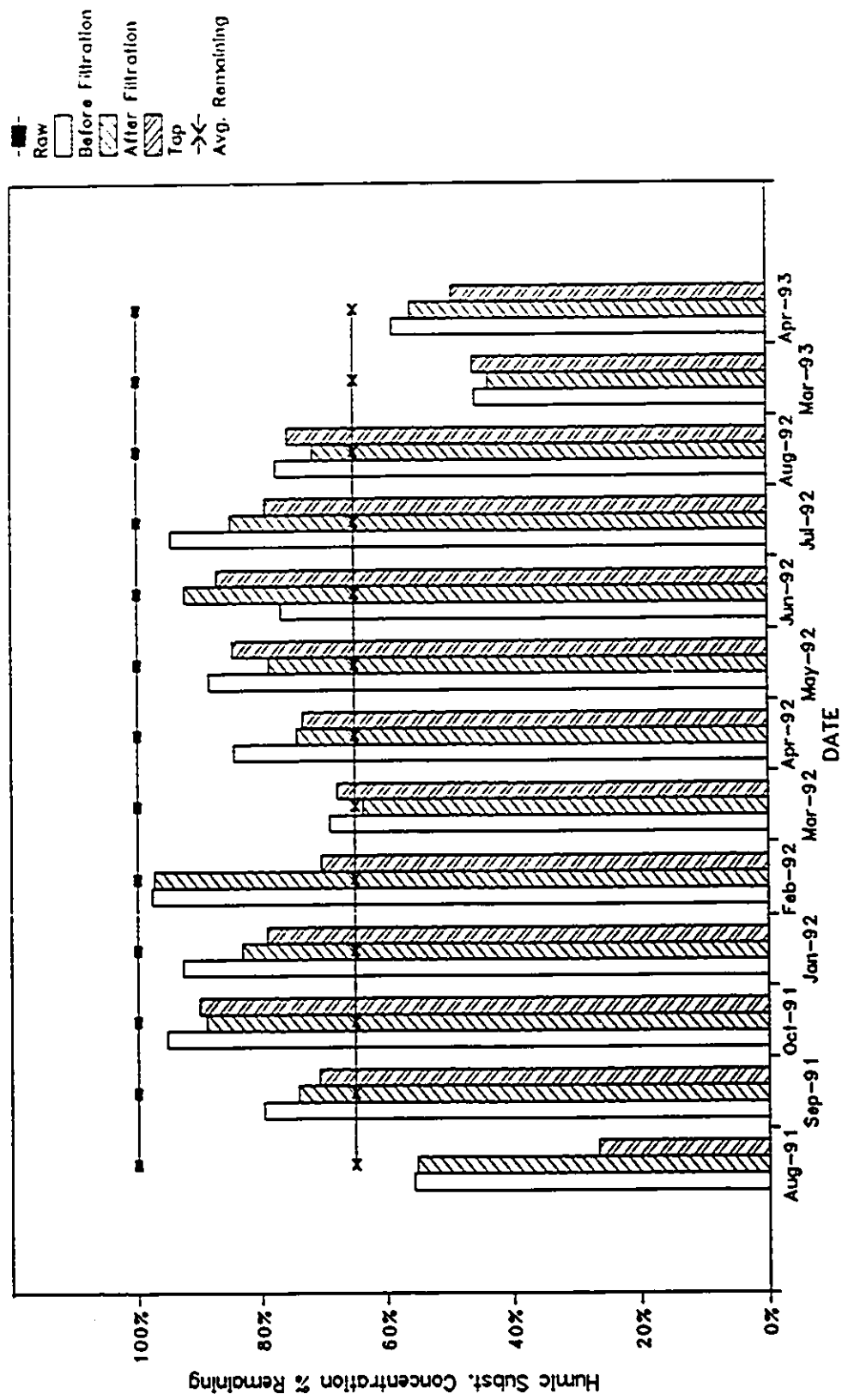


Figure 5.5. Removal behaviour of humic substances at the WWTP.

changes indicate that the plant is able to remove some DOC, including humic substances. The overall average removal of humic substances from the WWTP during this research period was 35 percent as shown in Table 5.2. Reports in the literature indicate removals of organic matter by conventional treatment plants from 29 to 68 percent (Collins *et al.*, 1985; Kim *et al.*, 1989).

From the results shown in Figure 5.5, it is observed that there is not always a consistent reduction in humic substances along the treatment process. This figure shows that (i) there is always a reduction in humic substances after the coagulation sedimentation process, (ii) the reduction after filtration is small, and (iii) after chlorination (tap water) the reduction is highly variable. The values for August 1991 and February 1992 show a marked decrease whereas values for September 1991, January 1991, April 1991, June 1991 and July 1991 show a slight decrease. A small increase was observed in October 1991, March 1992, May 1992 and August 1992. This can be attributed to a possible error in collecting a representative sample. Due to seasonal fluctuations in water demand, the hydraulic retention time had varied and probably the raw water samples did not correspond to the tap water samples. As noted in the literature (Glaze, 1987; Bablon *et al.*, 1991), the oxidation of humic substances by chlorine has a small effect on the DOC value. Consequently, it is difficult to determine the effect of the chlorination process on the removal of humic substances when measured as DOC.

Table 5.2. Removal behaviour of humic substances concentration at the WWTP.

Sample Date	Raw mg/L	Before Filtration mg/L	After Filtration mg/L	Tap mg/L
Aug-91	1.28	0.72	0.71	0.34
Sep-91	0.68	0.54	0.51	0.48
Oct-91	0.63	0.60	0.56	0.56
Jan-92	0.79	0.74	0.66	0.63
Feb-92	0.78	0.76	0.76	0.55
Mar-92	1.05	0.73	0.67	0.72
Apr-92	1.73	1.46	1.28	1.27
May-92	0.94	0.83	0.74	0.79
Jun-92	0.72	0.55	0.66	0.63
Jul-92	0.87	0.82	0.74	0.69
Aug-92	1.04	0.80	0.74	0.78
Mar-92	1.30	0.59	0.57	0.68
Apr-92	2.14	1.26	1.20	1.06
Average:	1.07	0.80	0.70	0.70

5.1.3. Apparent Molecular Size Distribution

Separation of a mixture of molecules of different sizes in a gel column occurs as a result of differences in the degree to which different molecules permeate the gel particles. Molecules larger than the gel pores move rapidly through the column with the eluent. Smaller molecules permeate the gel at a slower rate, depending on both their size and on the distribution of the gel particle size. As a result, large molecules emerge first from the bed, while smaller molecules are retarded.

For many groups of substances, a very close correlation is found between molecular size and elution behaviour and, for practical purposes, the molecular size is determined entirely by the elution volume. This is defined as the volume of eluent that is required to carry the molecules of the substance through the column.

The GPC was employed to determine the AMSD of the humic substances obtained from the different sampling points along the conventional water treatment train at the WWTP. The GPC chromatograms derived from the G-75 gel are presented in Appendix A. The chromatograms portray relative UVA at 254 nm as a function of the apparent molecular size.

The molecular size distributions were determined from the protein calibration curve. It is important to note that the molecular sizes calculated here are approximate or "apparent" molecular sizes. This is due to the fact that humic compounds are likely to have different structural characteristics than those of the calibration proteins and, therefore, likely to behave somewhat differently in the gel permeation process.

As indicated in Chapter IV, this particular gel provides an approximate molecular

size separation within the ranges of 3,000 to 80,000 for proteins and 1,000 to 50,000 for dextran. Molecules with a molecular size greater than the upper limit of the gel are "size excluded" from the infrastructure of the gel beads and are eluted at the void volume. Molecules with a molecular size of less than the lower limit are not chromatographically separated by this gel and are thus collectively eluted at an elution volume of slightly more than the total volume of the packed bed. The AMSD of the humic substances from the Detroit River water and treated water samples were within the gel limits separation for proteins.

A typical chromatogram of the humic substances from the raw water is presented in Figure 5.6. As can be observed in this Figure, the molecular size of the humic substances is apparently distributed into three components of different molecular size: a low size component from less than 3000 to 5,000, designated as Peak 3 (P-3); a middle molecular size component of 5,000 to 50,000 designated as Peak 2 (P-2) ; and a high molecular size component of more than 50,000, designated as Peak 1 (P-1). In general the same distribution was observed for all the samples collected in this study. This indicates that practically the same composition of humic substances was present through the study period.

Adsorption of organics to the gel was minimal in this study. An average of 93% of DOC was recovered from the gel column for all humic solutions tested. A range of 0-13 percent loss of organics by adsorption to the gel has been reported by other investigators (Schnoor *et al.*, 1979).

Table 5.3 provides some of the molecular size distributions of different humic

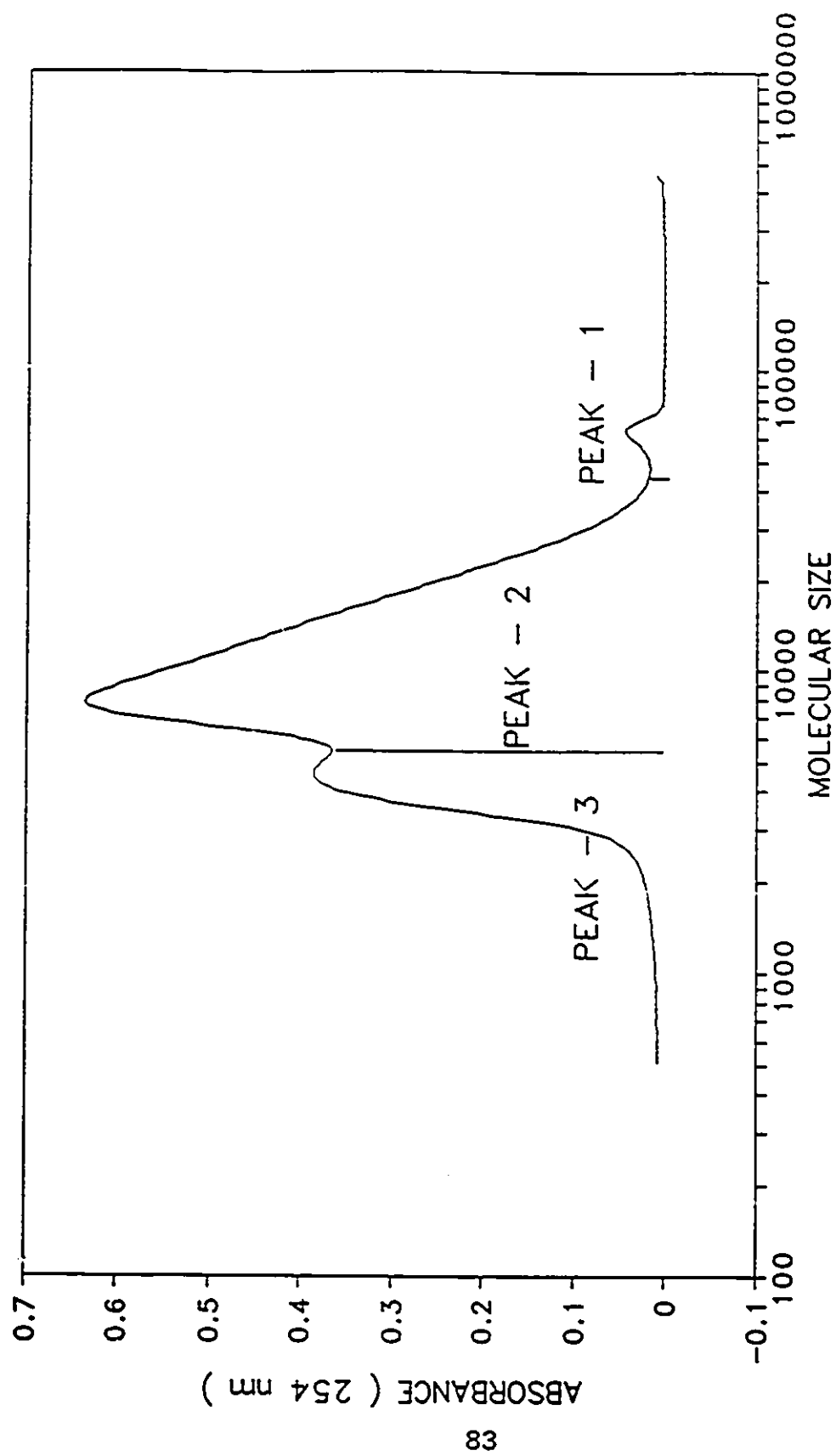


Figure 5.6. Typical AMSD of humic substances from the water source (raw water).

Table 5.3. AMSD of humic substances from different sources.

Author	Source	MOLECULAR SIZE RANGE			Method of Determination
		Low (% of Total)	Medium (% of Total)	High (% of Total)	
Gjessing and Lee (1967)	Norwegian Lakes	< 5,000 (33%)	5000-20,000 (67%)		GPC
Kemp and Wong (1974)	Ontario and Erie Lakes Fulvic Acid (sediments)	< 700 (20%-23%)	5,000-10,000 (23%-35%)	> 200,000 (18%-29%)	GPC
Schnoor <i>et al.</i> , (1979)	Iowa River	< 1,000 (7%)	1,000-3,000 (83%)	> 50,000 (1%)	GPC
Lee (1980)	Peat Fulvic Acid	< 1,000 (39%)	1,000-50,000 (53%)	> 50,000 (9%)	GPC
Veenstra and Schnoor (1980)	Iowa River	< 1,000 (14%)	1,000-5,000 (86%)		GPC
Thurman <i>et al.</i> , (1982)	Swannee River Humic Acid		5,000-10,000 (100%)		Small-angle X - ray Scattering
	Swannee River Fulvic Acid	1,000-1,500 (100%)			
El-Rehaili and Weber (1987)	Aldrich Humic Acid	< 3,000 (38%)	3,000-40,000 (57%)	> 40,000 (5%)	GPC
	Fulka Humic Acid	< 3,000 (28%)	3,000-40,000 (63%)	> 40,000 (9%)	
	Contech Humic Acid	< 3,000 (25%)	3,000-40,000 (72%)	> 40,000 (3%)	
	Huron River Water	1,000-6,000 (98%)			
Amy <i>et al.</i> (1988)	Biscayne Aquifer	< 500 (48%)	10,000-20,000 (19%)	> 40,000 (12%)	Ultrafiltration
		500-10,000 (6%)	20,000-40,000 (19%)		
This research	Detroit River	< 5,000 (32%)	5,000-50,000 (64%)	> 50,000 (4%)	GPC

substances reported by other investigators using GPC, UF and small angle X-ray scattering. A comparison is difficult because of the lack of a standard methodology for the determination, the sensitivity of GPC to pH variations, and the different methods used for the concentration of humic substances before analysis. However, after analyzing these results, it was observed that the highest percent of humic substances, 64%, corresponds to the medium molecular size (5,000-50,000) fraction, P-2. The second percentage, 32%, corresponds to the low molecular size (< 5,000) fraction, P-3 and the third percentage, 4%, corresponds to the high molecular size (> 50,000) fraction, P-1. These ranges agree with the ranges reported by the other researchers (Kemp and Wong, 1974; Gjessing and Lee, 1967; Lee, 1980).

5.1.4. AMSD and Removal of Humic Substances Through Conventional Treatment Processes

The GPC was employed to investigate the apparent removal of the different molecular size fractions of humic substances by each treatment process in the conventional treatment.

The degree to which humic materials absorb UV light was the basis for quantifying the amount of humic material removal as a function of AMS distribution by the conventional treatment of drinking water. Implied in this analysis is that humic substances in the high molecular size range absorb UV light to the same extent as those in the low molecular size range on a unit mass basis. This assumption was based on the consideration that the relative absorbance in a particular fraction is more important than

the absolute value. The relative difference in normalized UV absorption between untreated and treated waters provided the data needed to evaluate the performance of the treatment processes and detected which fractions of aquatic humic substances were most affected in the conventional treatment process.

5.1.4.1. Prechlorination and Coagulation

Figures 5.7 show the typical effects of prechlorination and coagulation-sedimentation processes on the removal of humic substances. Table 5.4 displays the averages of the relative reduction of humic substances with respect to the raw water in each molecular size range (P-1, P-2 and P-3). During the sampling from July 1991 to August 1992, the first peak, corresponding to the high molecular size was reduced by 76 percent, the second peak, identified as medium molecular size, was reduced by 40 percent and the third peak corresponding to low molecular size was reduced by 29 percent. The average reduction of the total area, over 12 months, was 37 percent. It was observed from the different chromatograms obtained during this study that 50 percent of the samples showed a very small fourth peak in the low molecular size of less than 400. This peak was not observed in the raw water samples. Hence, the occurrence of this peak was probably due to the oxidation action of chlorine on the organic matter at the prechlorination stage.

5.1.4.2. Filtration

After filtration, the reduction in humic substances detected by UVA was only 1 percent on average for the high molecular size (P-1) and 4 percent on average for the

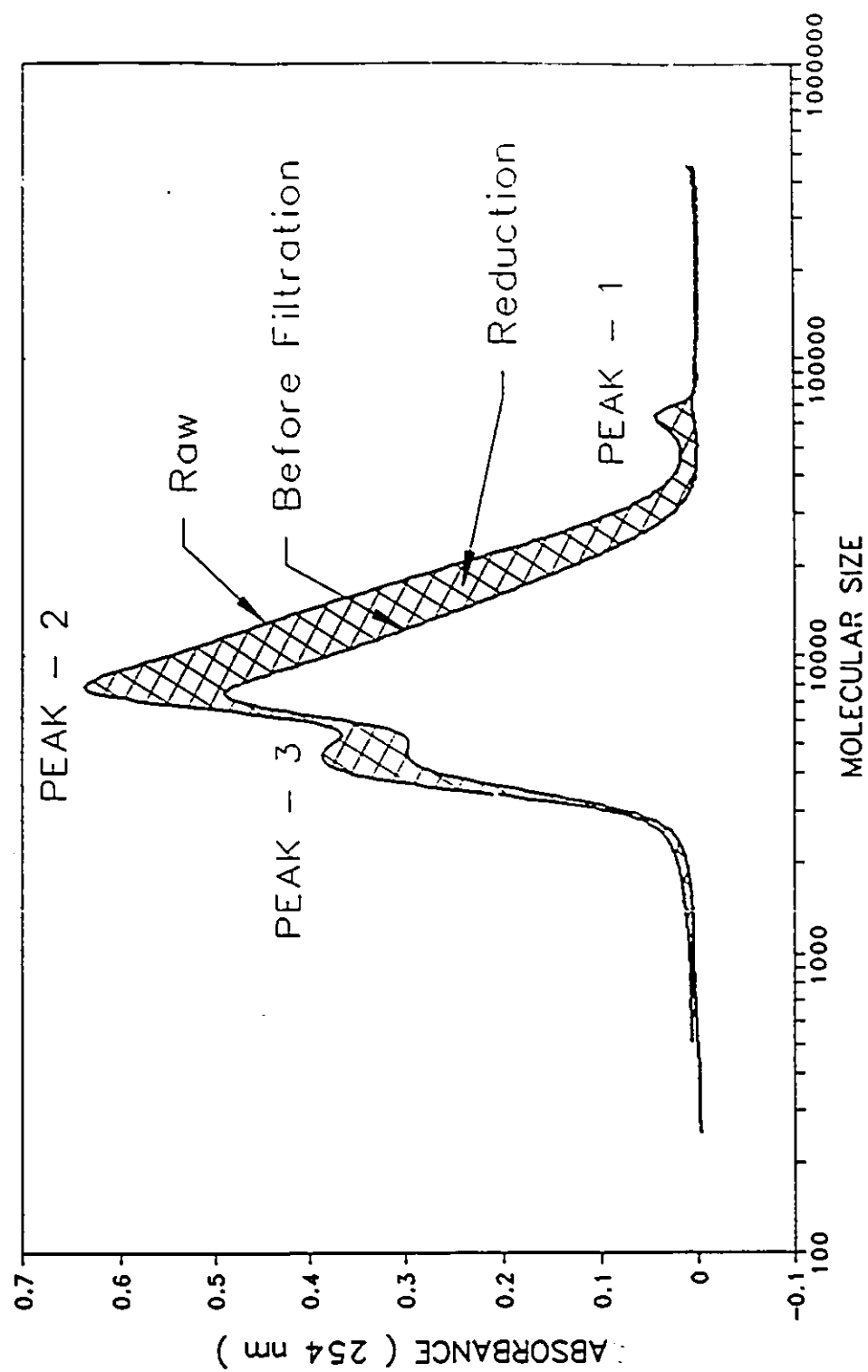


Figure 5.7. Typical reduction of humic substances after prechlorination and coagulation-sedimentation processes.

Table 5.4. Relative reduction in the three different molecular size ranges during the treatment processes.

DATE	PEAK 1			PEAK 2			PEAK 3		
	Before Filtration (%)	After Filtration (%)	Tap Water (%)	Before Filtration (%)	After Filtration (%)	Tap Water (%)	Before Filtration (%)	After Filtration (%)	Tap Water (%)
Jul. 91	96	99.2	99.9	31.2	57.1	61.4	-21.8*	27.9	34.4
Aug. 91	84.9	69.6	88.2	57.1	35.7	72.1	-31.2*	-9.7*	-47.8
Sep. 91	92.5	88.3	89.8	31.3	38.8	51.6	50.7	52.9	51.6
Oct. 91	100	89.4	66.8	15.5	29.6	20.2	33.5	26.1	-8.6*
Jan. 92	89.2	72.5	85.4	36.4	39.8	66.2	64.6	59.9	74.7
Feb. 92	69.1	67.4	89.2	30.1	31.5	69.9	16.5	28.8	28.2
Mar. 92	96.4	93.2	96.5	60.4	64.5	55.9	34.3	43.4	29.7
Apr. 92	84.6	91.2	85.2	27.2	39.2	45.2	33.6	28.6	27.7
May. 92	70.3	94.4	82.9	51.5	50.2	48.1	1.5	21.8	30.5
Jun. 92	59.8	57.5	9.3	64.4	47.3	55.2	79.9	65.7	75.2
Jul. 92	66.4	25.1	60.6	15.4	30.1	41.9	30.4	34.5	45.1
Aug. 92	4.1	71.9	58.8	59.3	60.2	62	57.3	59.1	58.2
Average Reduction	76	77	76	40	44	54	29	37	41
Reduction between processes	76	1	-1	40	4	10	29	8	4

* Negative reduction indicate an increase in the area with respect to raw water.

medium molecular size (P-2). The low molecular size (P-3) showed on average a decrease of 8 percent (Table 5.4). The reduction of the total area, averaged over 12 months for this process, was 4 percent. These low reductions can be interpreted as a result of the process itself, since conventional filtration will retain only the large particles, approximately 2 microns and above in diameter. Although most humic substances are present in the dissolved fraction, less than $0.45\ \mu$, some may be retained, probably by adsorption on, colloidal particles.

5.1.4.3. Chlorination

After chlorination, a reduction of the area corresponding to the medium and low molecular size range (P-2 and P-3) was observed. Average reductions of 10 and 4 percent respectively were detected (Table 5.4). However no reduction was detected in the area of the high molecular size, P-1. The average reduction of the total area over 12 months for this process was 8 percent. The effects of chlorine on the humic substances are reflected by the reduction of the areas corresponding to the medium and low molecular sizes. The low dosages of chlorine used in chlorination were not expected to reduce the humic substances concentration. However, the decrease in the UVA may be attributed to the possible changes in the structural characteristics of the humic substances caused by the destruction of chromophoric sites by chlorine.

Figure 5.8 shows the AMSD chromatograms where the maximum value for each peak from the higher to the lower molecular sizes shifted slightly. This observation has been reported by other researchers (Chadik and Amy, 1987).

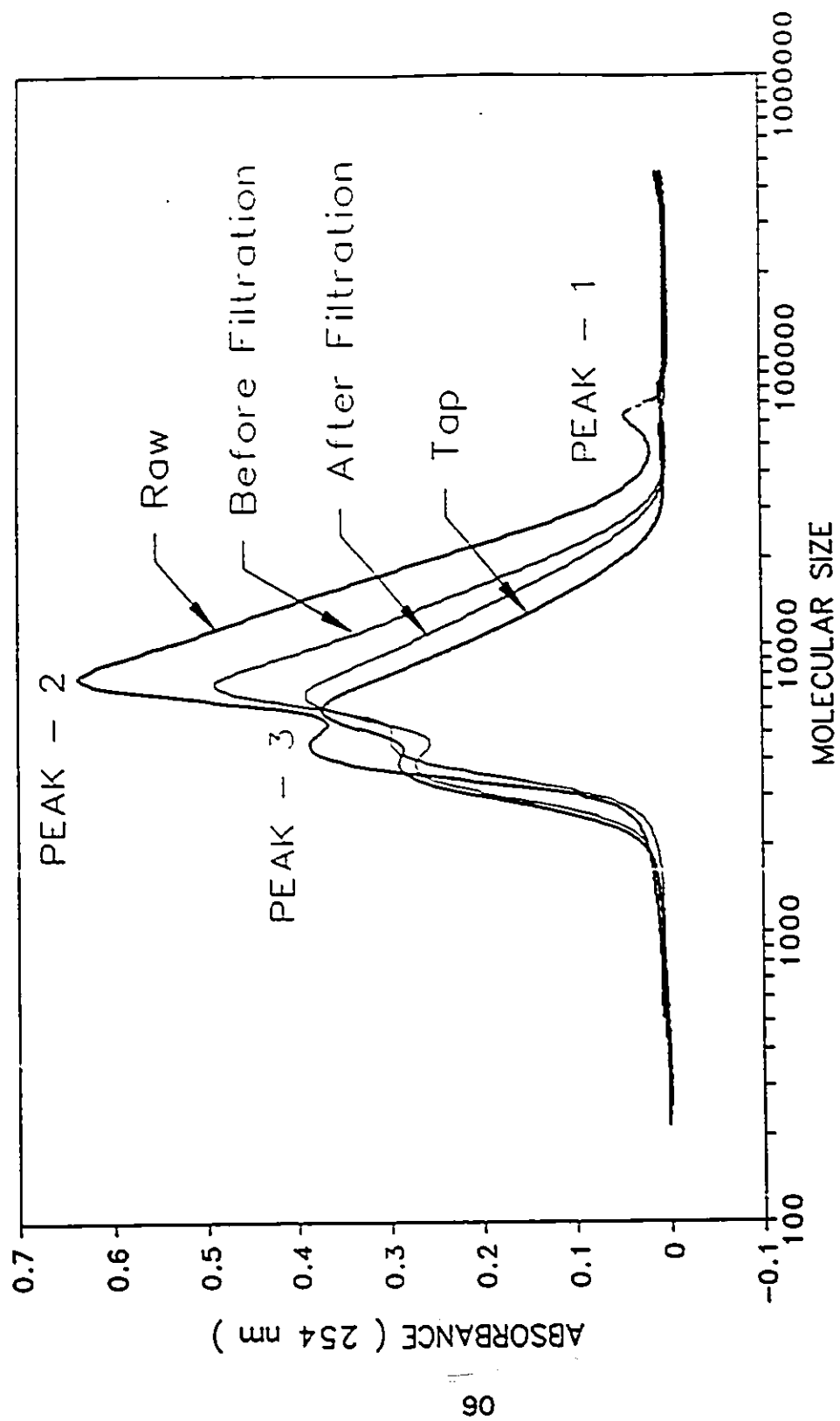


Figure 5.8. Typical AMSD of humic substances along water treatment processes.

The relative compositions of the samples for the three different components in the raw and treated water are shown in Figure 5.9. As mentioned earlier, each treatment process had reduced the three different peaks and a small peak in the low molecular size had appeared in some samples. However, the relative composition of samples from different stages of treatment remained practically the same.

5.1.5. Trihalomethane Formation Potentials (THMFP)

In order to determine the reactivity, expressed as μg of THM/mg of C, of the Detroit River water to form THMs and the effect of the conventional treatment process on the THMFP, water samples taken during the months of March and April 1993, were chlorinated and analyzed for THMs using the methods described in Chapter IV. In the first step of analysis, samples were characterized (Table 5.5) with respect to DOC, UVA, pH, turbidity, residual chlorine and instantaneous THMs (THM(ins)). As expected, the THM(ins) for raw water was zero. Since the prechlorination takes place in the rapid mix units before coagulation, all other samples showed an initial concentration of THMs. The turbidity in these two months were high.

The second step included the concentration of humic substances, the determination of the AMSD and the fractionation of the humic substances. Following this, the chlorine demand for each sample and their corresponding non-humic fractions were determined. Because of the small volumes of sample, the chlorine demand from the fractionated and concentrated humic substances was not determined. As indicated in the general procedure, the DOC and the UVA measurements were done for all the samples. Finally,

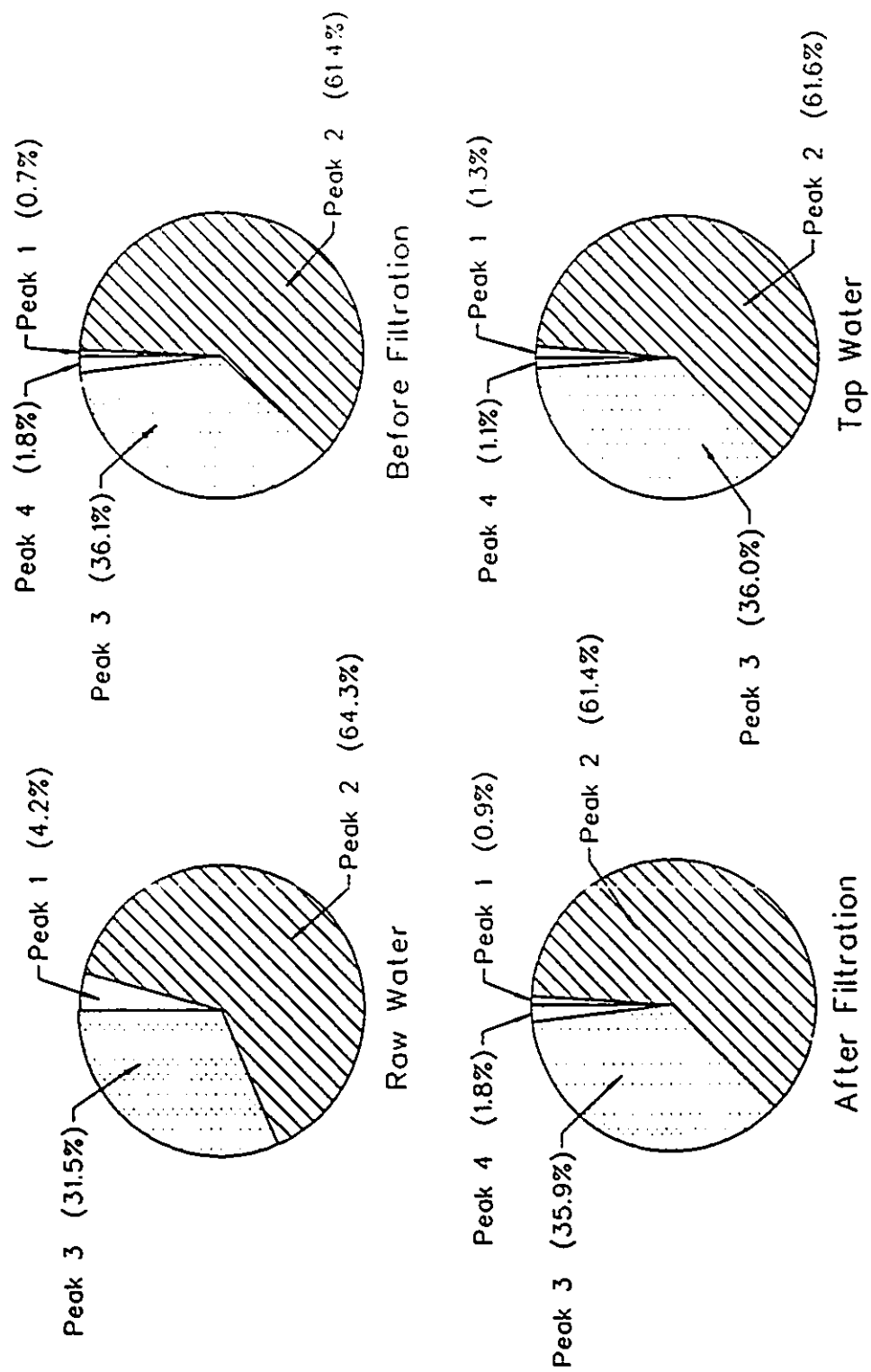


Figure 5.9. Relative distribution of different molecular size compounds from the different stages of treatment.

Table 5.5. Characterization of untreated and treated water samples, March and April 1993.

Sample	DOC mg/L	UVA abs units	Turbidity units	pH	Chlorine residual mg/L	THMs (inst) µg/L	Humic Substances mg/L
M a r c h	Raw	0.056	2.7	7.8			1.30
	Before Filtration	0.055	2.7	7.1	1.7	30	0.59
	After Filtration	0.023	1.01	7.0	1.1	31	0.57
	Tap	0.027	0.31	7.0	1.1	29	0.60
A p r i l	Raw	0.320	33.6	7.7			2.14
	Before Filtration	0.057	2.66	7.4	1.5	26	1.26
	After Filtration	0.034	0.475	6.9	1.1	26	1.20
	Tap	0.031	0.37	7.0	1.1	29	1.06

samples were chlorinated, incubated for 7 days and the amount of formed THMs measured

5.1.5.1. Chlorine Demand

All samples and their corresponding non-humic fractions, for March 1993, were chlorinated with an initial chlorine dosage of 25 mg/L, buffered to pH 7 and maintained at a constant temperature of 25°C for 7 days. After this time, the residual chlorine was measured and the consumed chlorine was determined. Table 5.6 shows the results of these determinations. Similarly, all the samples, and their corresponding non-humic fractions for April 1993 were chlorinated and instead of only one measurement at the end of 7 days, measurements of residual chlorine were made at 0.2, 1, 2, 4 and 7 days. Figures 5.10 and 5.11 present the rate of chlorine consumption for the various samples collected in April 1993.

The consumption of chlorine by both overall samples and non-humic fractions appears to follow an exponential curve, showing the highest rate of consumption in the first few hours and then decreasing with time. After the seventh day, it appears that organic matter is still consuming chlorine in the raw and before-filtration samples. However, after-filtration and tap water samples did not consume any more chlorine. For the non-humic fractions, after the second day the residual chlorine remained almost constant, indicating that the organic matter was exhausted or the consumption rate was extremely low. As expected, the overall samples consumed approximately 60 percent more chlorine than their corresponding non-humic fractions.

Table 5.6. Chlorine consumption for March and April 1993 samples.

		March 1993 Cl ₂ consumed mg/L	April 1993 Cl ₂ consumed mg/L
S a m p l e	Raw	9.3	14.6
	Before Filtration	6.2	7
	After Filtration	5.5	5.8
	Tap	5.5	5
	Blank	1.7	1.7
N o n H u m i c	Raw	3.5	6.0
	Before Filtration	2.8	3
	After Filtration	2.5	2
	Tap	2.5	2
	Blank	1.7	1.6

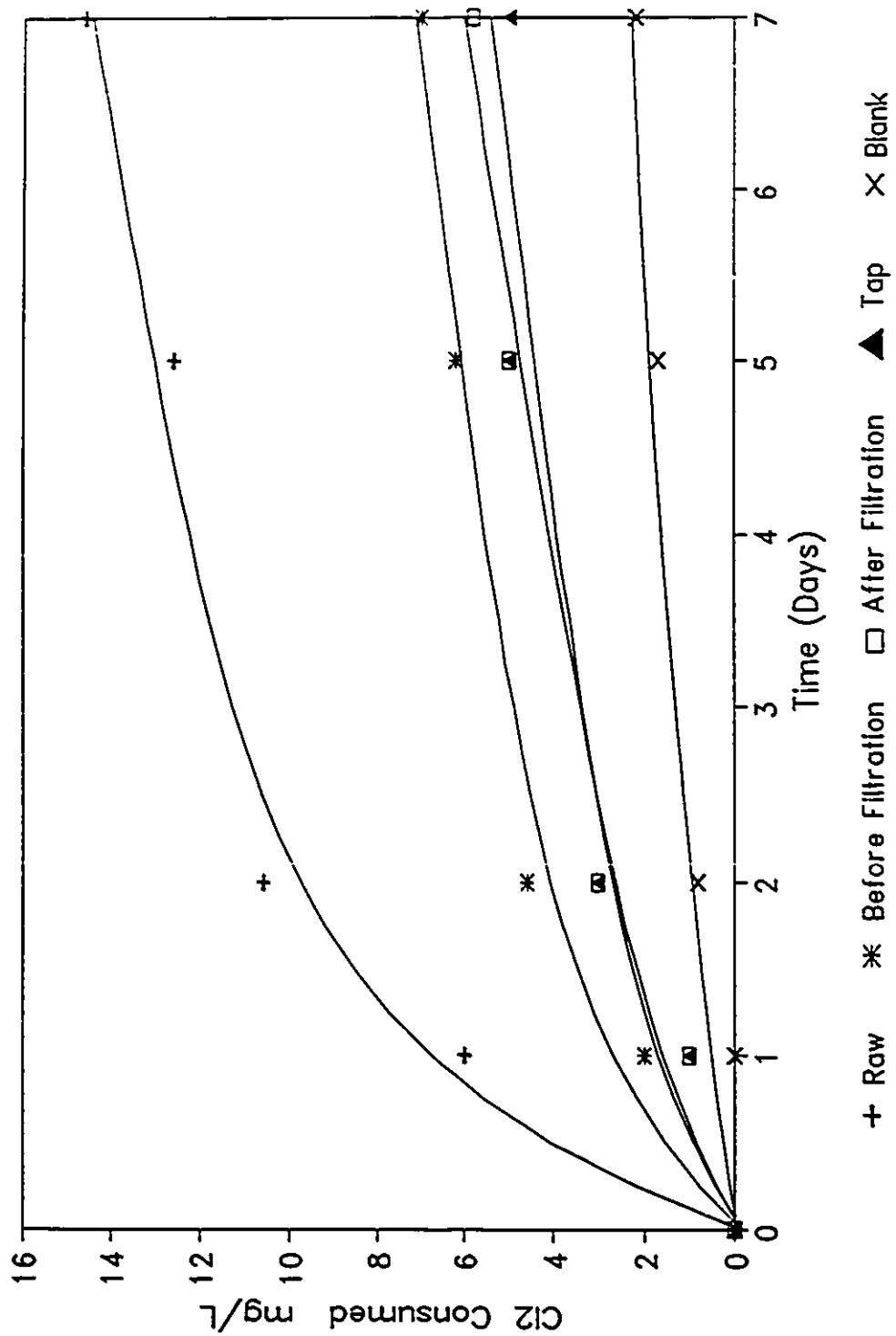


Figure 5.10. Chlorine consumption rate by samples taken in April 1993.

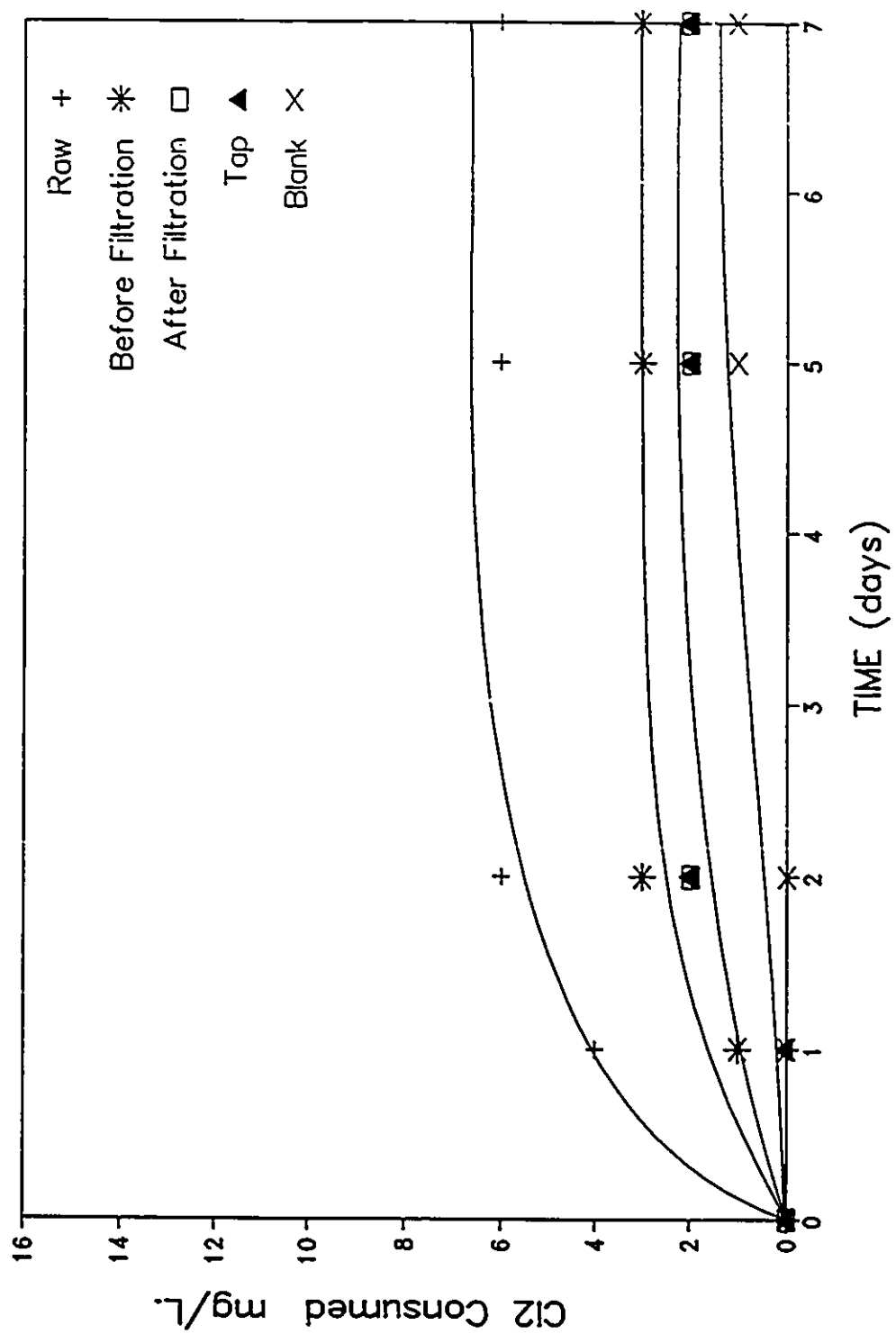


Figure 5.11. Chlorine consumption rate by non-humic fractions.

5.1.5.2. THMFP for Overall Samples and their Corresponding Non-Humic Fractions

Table 5.7 presents the results from the THMFP measurements of the untreated and treated waters and their corresponding non-humic fractions. It is reported in the literature that all conventional treatment processes reduce the THMFP of untreated water. Also, it is reported that the non-humic fraction has a lower THMFP than their corresponding overall samples. The THMFP for the non-humic fraction in the present study was almost 50 percent of the overall sample THMFP and thus constituted an important fraction of the THMFP. The chlorinating conditions of the overall sample were the same as for the non-humic fraction. In order to determine the maximum potential for both, i.e., the overall sample and the non-humic fraction, the same chlorine dosage was used. It is known from the literature that the reaction of chlorine with organic matter is very complex and an increase in the chlorine dosage may result in increased yield of THMs. This may be the reason for obtaining such high THM reactivities for the non-humic substances. In the case of the Detroit River water, the DOC fraction of the non-humic substances was observed to constitute on average 70% of the total DOC. Hence, it can be concluded that the DOC fraction of the non-humic substances plays an important role there in the formation of THMs. Since the humic fraction has always been characterized as the major contributor in THM formation, few studies have reported the contribution of the non-humic substances to the THMFP. Collins *et al.*, (1986) characterized the non-humic content of several waters in the USA. He observed that these fractions contributed as much as 65% of the NVTOC and 56% of the THMFP associated

Table 5.7. THMFP of untreated and treated water samples and their corresponding non-humic fraction.

	Sample				Non-Humic Fraction			
	DOC (mg/L)	THMFP (μ g/L)	THM/DOC (μ g/mg)	DOC (mg/L)	THMFP (μ g/L)	THM/DOC (μ g/mg)		
M a r c h	Raw	64	26	1.8	37	21		
	Before Filtration	55	26	1.8	26	14		
	After Filtration	24	13	1.5	12	8		
	Tap	19	11	1.5	9	6		
A p r i l	Raw	104	33	2.1	53	25		
	Before Filtration	97	39	1.8	38	21		
	After Filtration	93	40	1.7	53	31		
	Tap	81	35	1.7	38	22		

with Colorado River water.

5.1.5.3. THMFP from Humic Fractions

The fractionation of humic substances by molecular size using GPC has been reported by many researchers, although a consistent methodology is lacking. The investigation of THM production from the various humic fractions after chlorination has been reported by different researchers (Schnoor *et al.*, 1979; Oliver and Visser, 1980; El-Rehaili and Weber, 1987). However, as indicated in the literature review, there is no clear agreement as to which fractions, smaller or larger sizes, humic or fulvic acids are the major contributors to THM formation.

In this research, concentrated humic substances from the samples collected in March and April 1993 were fractionated by GPC. These fractions were characterized and analyzed using the general procedures and methods described in Chapters III and IV. The range limits of fractionation were based on the three distinct peaks observed previously in all the chromatograms for AMSD characterization during the period between July 1991 to August 1992. Since GPC fractionation is highly affected by pH, which in turn could also affect the THMFP, the samples were analyzed in both forms: the sodium and acid forms of humic substances. The AMSD chromatograms under different conditions are shown in Figures 5.12 to 5.15. The AMSD chromatograms of the concentrated acid form of humic substances, as can be seen in Figures 5.13 and 5.15, show only one peak in the approximate range of the AMSD chromatogram of the humic substances in the sodium form. Therefore, the total area was divided into three fractions observed in the

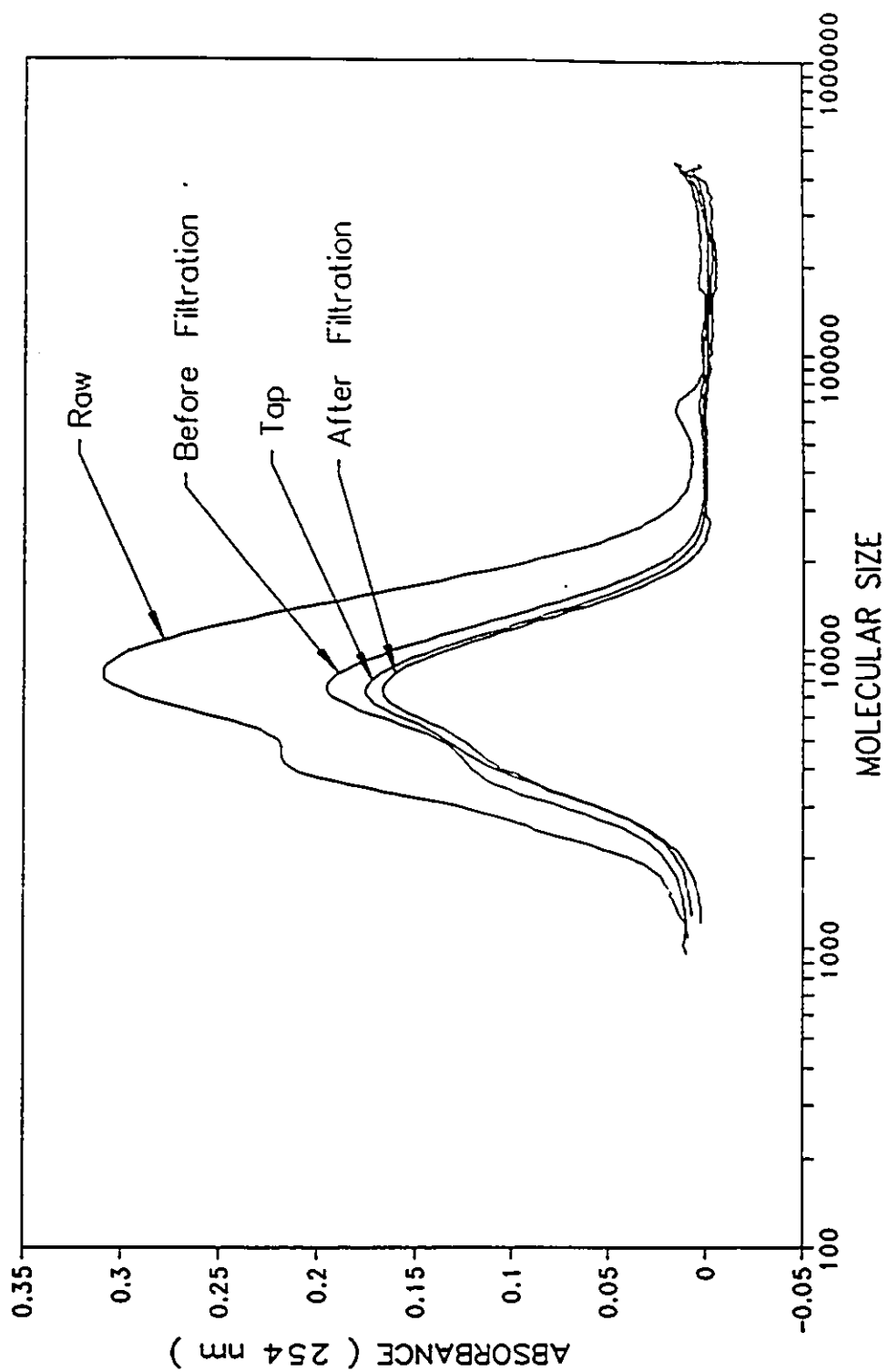


Figure 5.12. GPC-AMSD of humic substances, sodium form, March 1993.

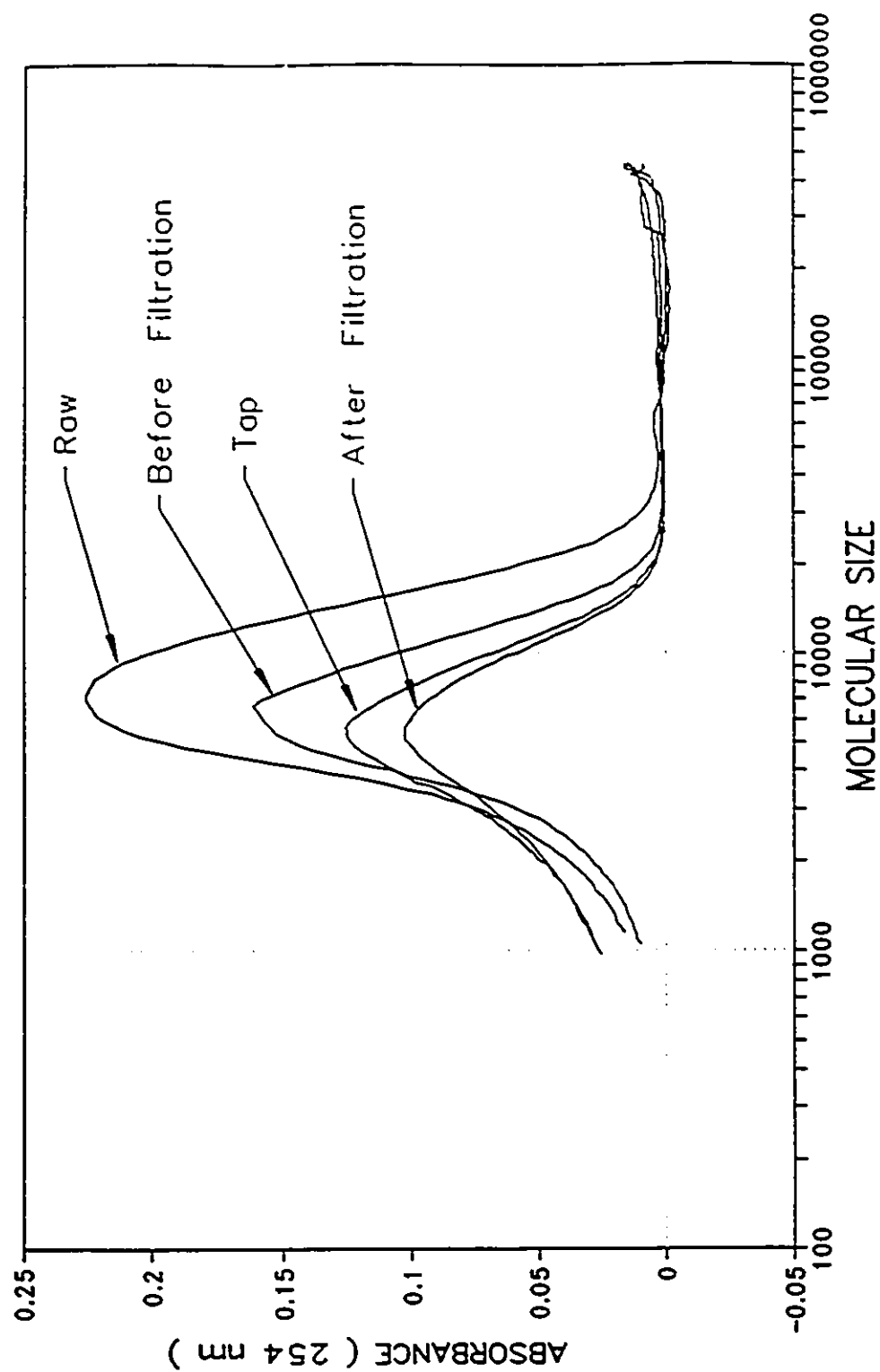


Figure 5.13. GPC-AMSD of humic substances, acid form, March 1993.

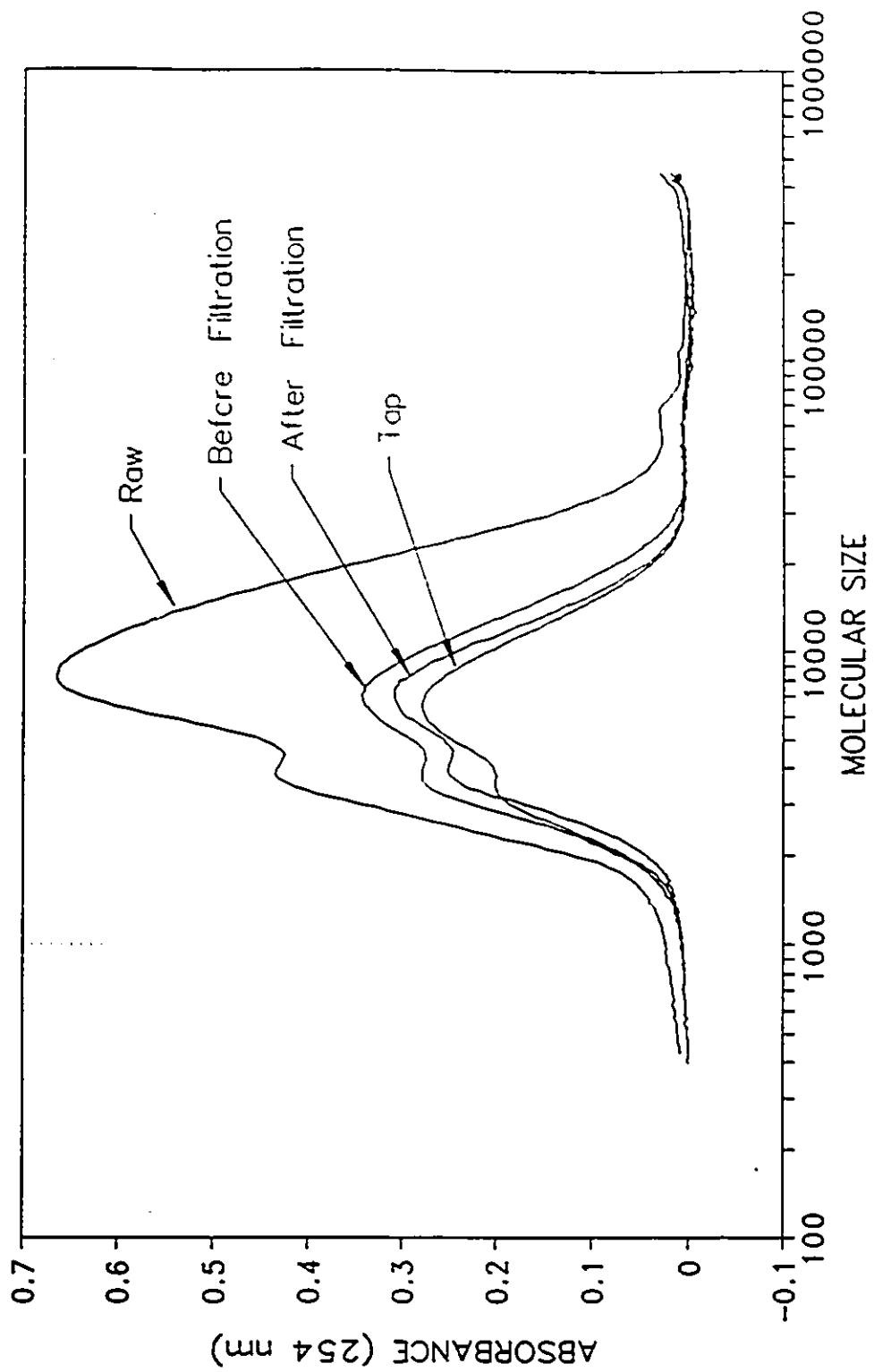


Figure 5.14. GPC-AMSD of humic substances, sodium form, April 1993.

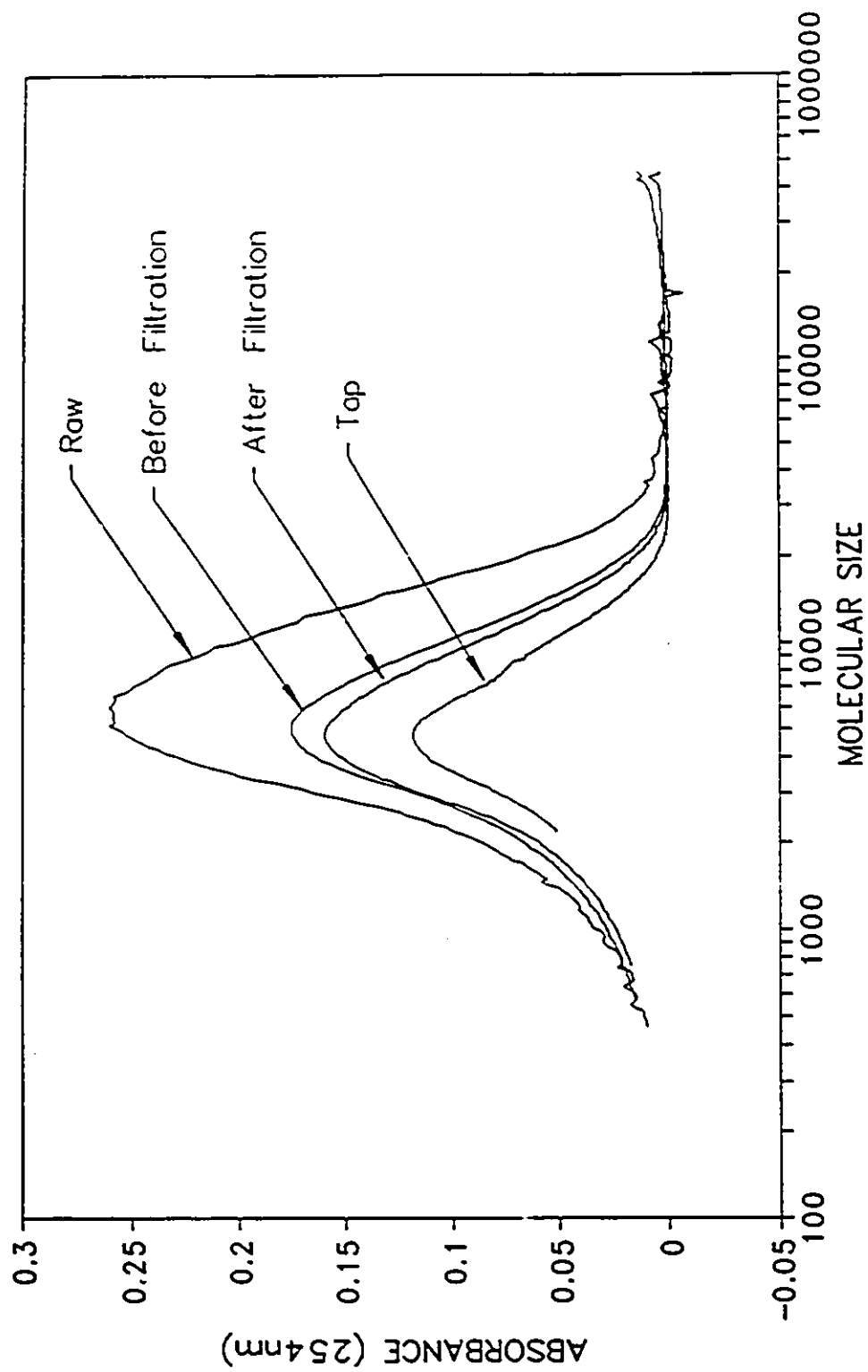


Figure 5.15. GPC-AMSD of humic substances, acid form, April 1993.

sodium form (Figures 5.12 and 5.14). Different fractions from all samples collected in April 1993 were analyzed for DOC values to obtain information on the comparison between the UVA at 254 nm and the corresponding DOC values. The AMSD with corresponding DOC values are presented in Figures 5.16 and 5.17. It is evident that the concentration of DOC at the different elution volumes from the fractionated sample depicts in general the same AMSD obtained by UVA analysis. The UVA of a sample could be measured in seconds, whereas every DOC determination took at least 30 minutes. Therefore, the number of points available to describe the DOC for different AMSD was limited. Results from the DOC and UVA determinations are plotted in Figure 5.18 and a correlation coefficient of 0.84 was obtained. It should be recognized that the data points in Figure 5.18 are the average for each of the three peak ranges for four different stages of treatment. The data show a direct correlation between UVA and DOC of the sample.

All the fractions from different molecular size fractions identified previously by GPC were chlorinated and analyzed for THMs after a 7 day period to determine their reactivity. Results for the THMs formed and the chlorine consumed, for each fraction, are presented in Figures 5.19 to Figure 5.22. However, no specific trend was observed. There is no clear difference for the influence of the pH on the fractionated sample in the THMFP of the fractions. Analyzing the chlorine consumption and the THMs formed, there is a trend observed in some fractions, but it is not consistent. The random nature of the results obtained in this experiment can be attributed to the fact that, due to instrument limitations, the THM analyses were made two months after the chlorine

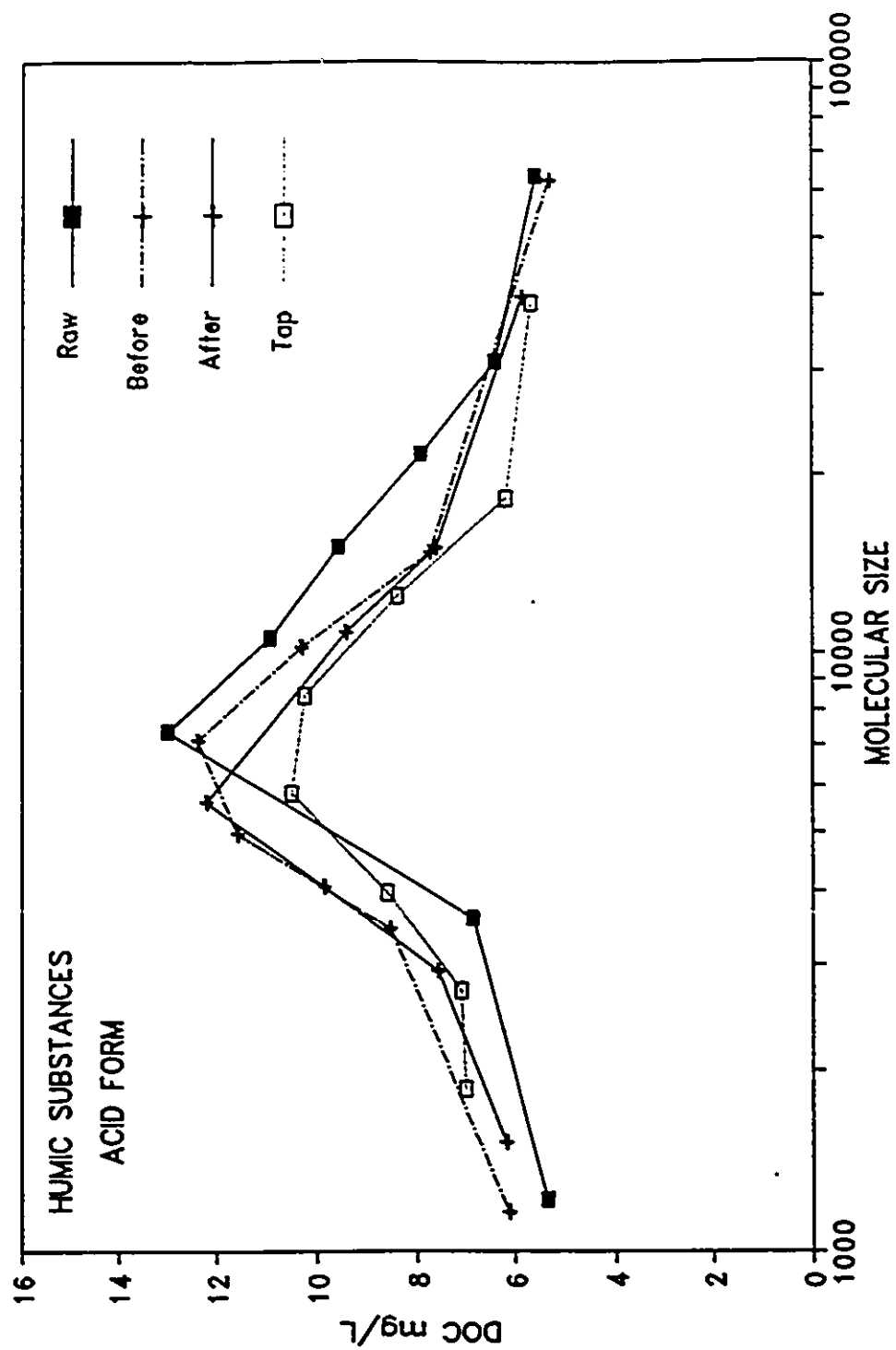


Figure 5.16. DOC-AMSD of humic substances, acid form, April 1993.

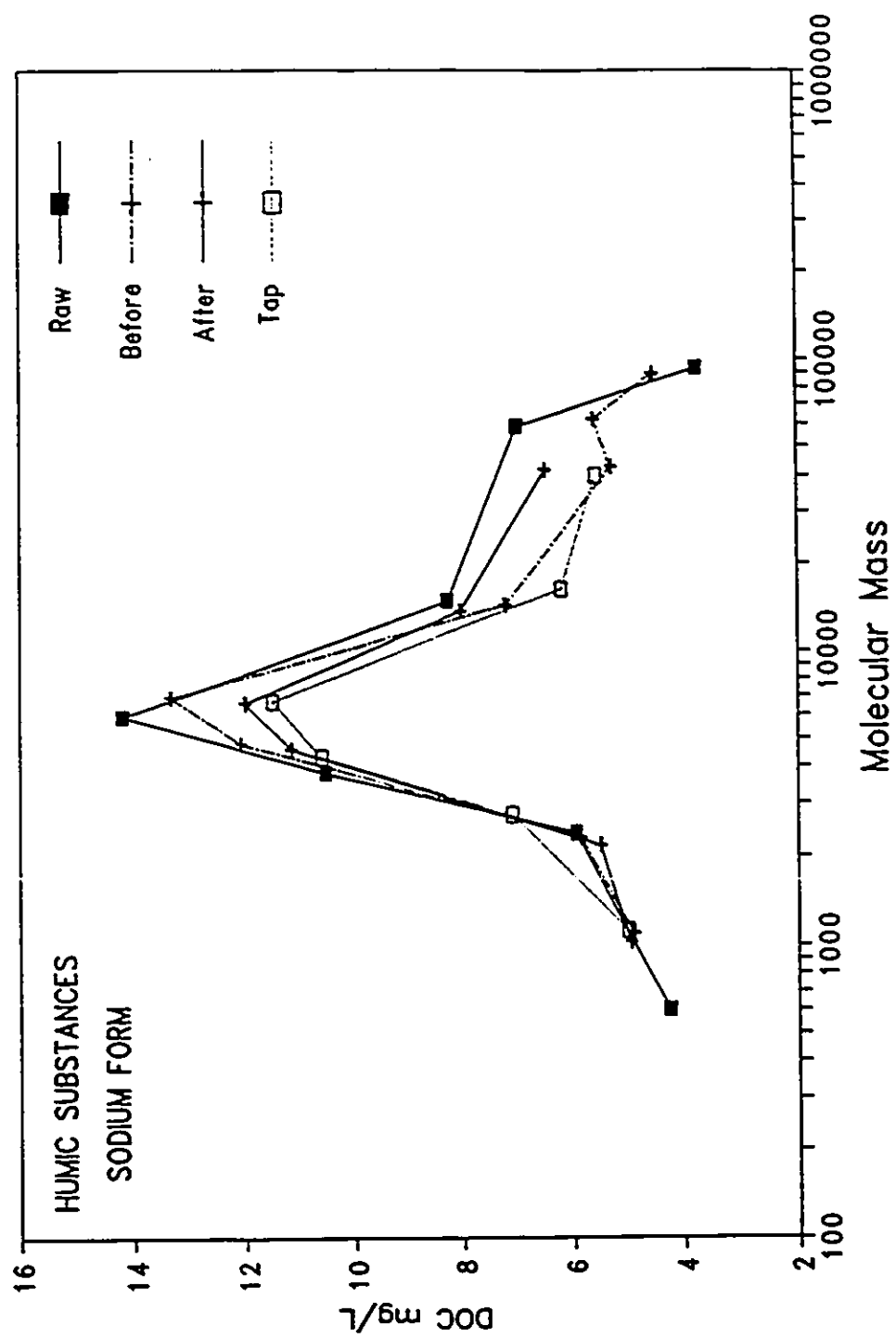


Figure 5.17. DOC-AMSD of humic substances, sodium form, April 1993.

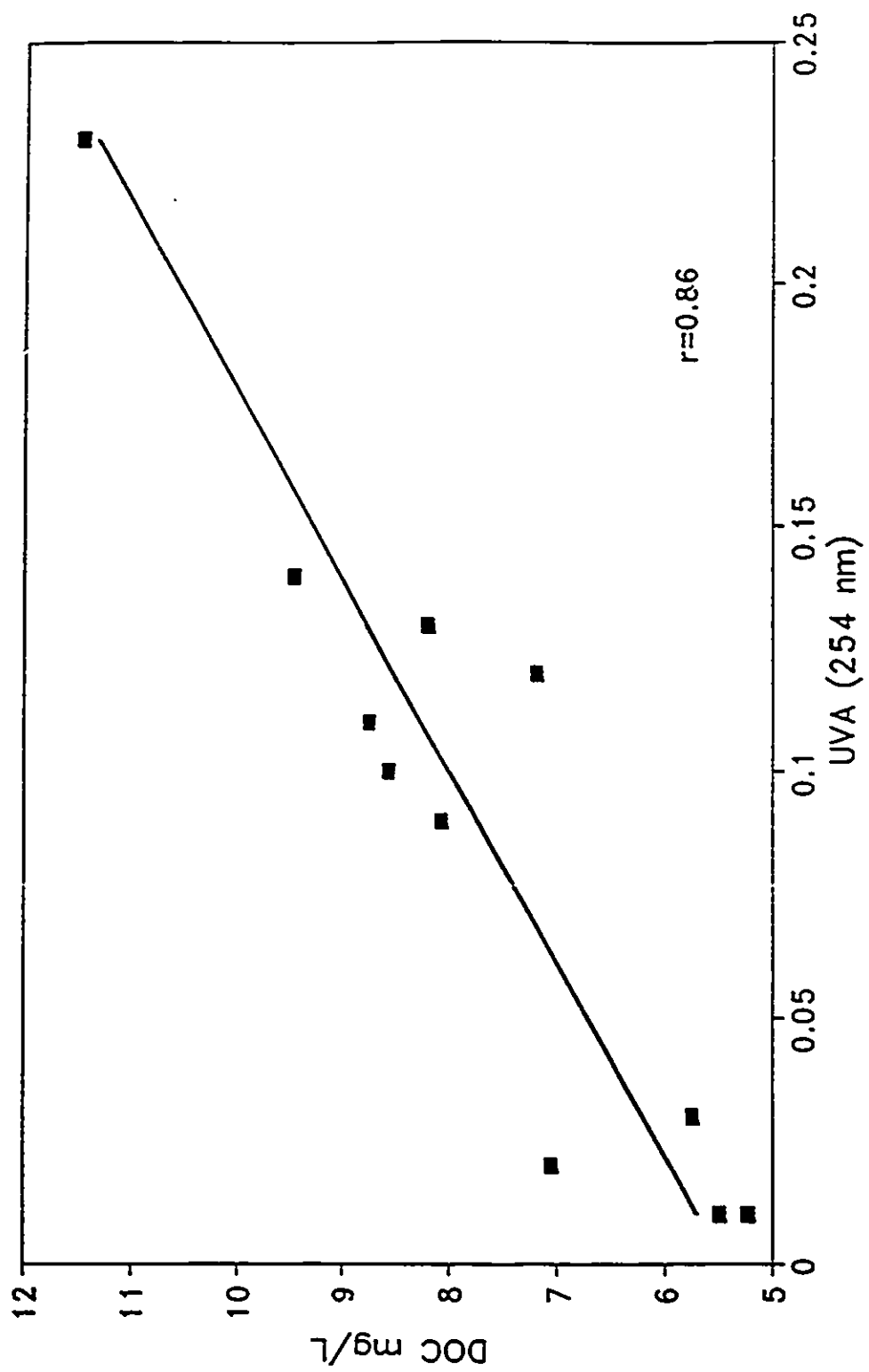


Figure 5.18. DOC vs. UVA correlation between different sample fractions.

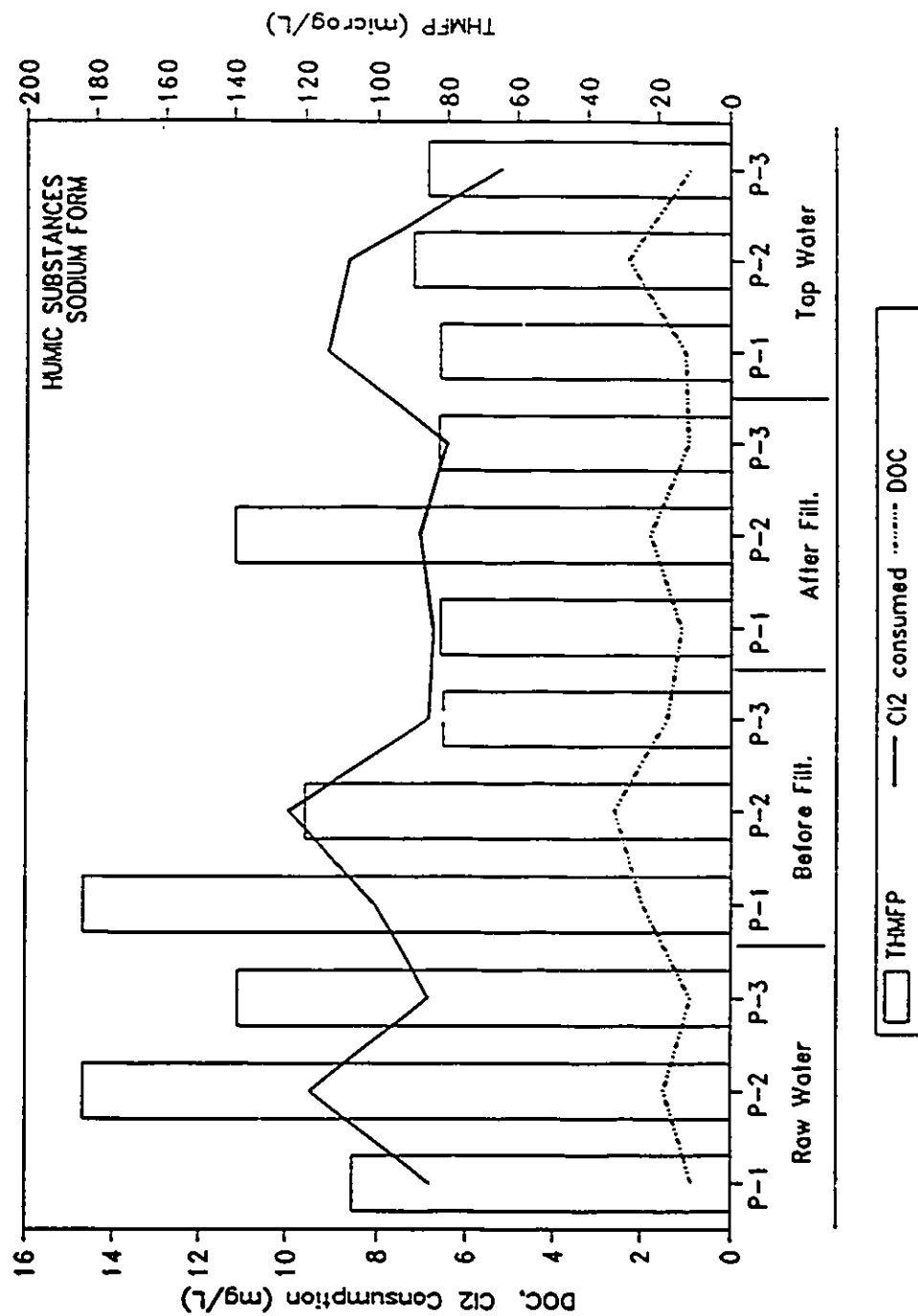


Figure 5.19. THMFP, DOC and chlorine consumption characterization of fractionated samples, March 1993 (sodium form).

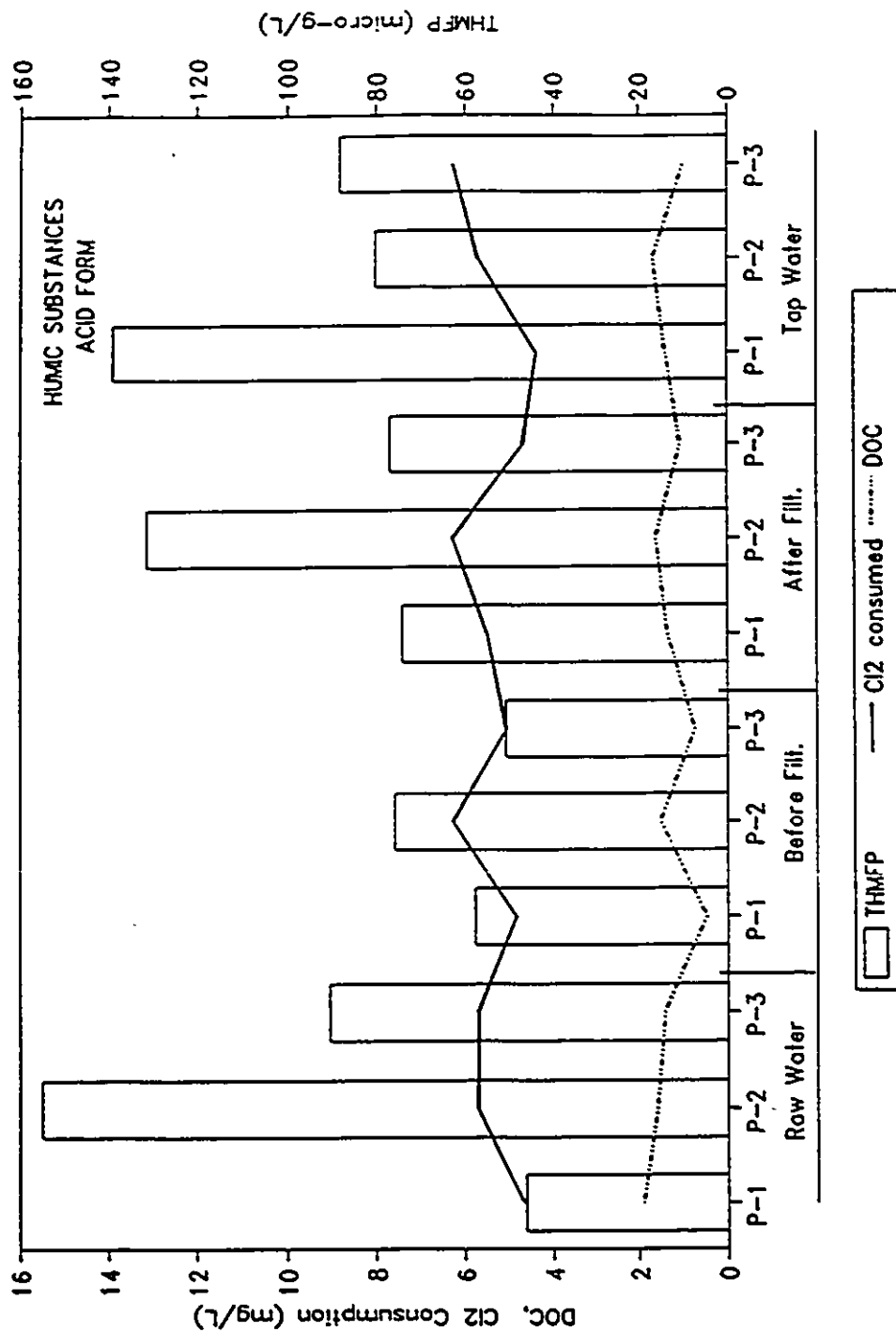


Figure 5.20. THMFP, DOC and chlorine consumption characterization of fractionated samples, March 1993 (acid form).

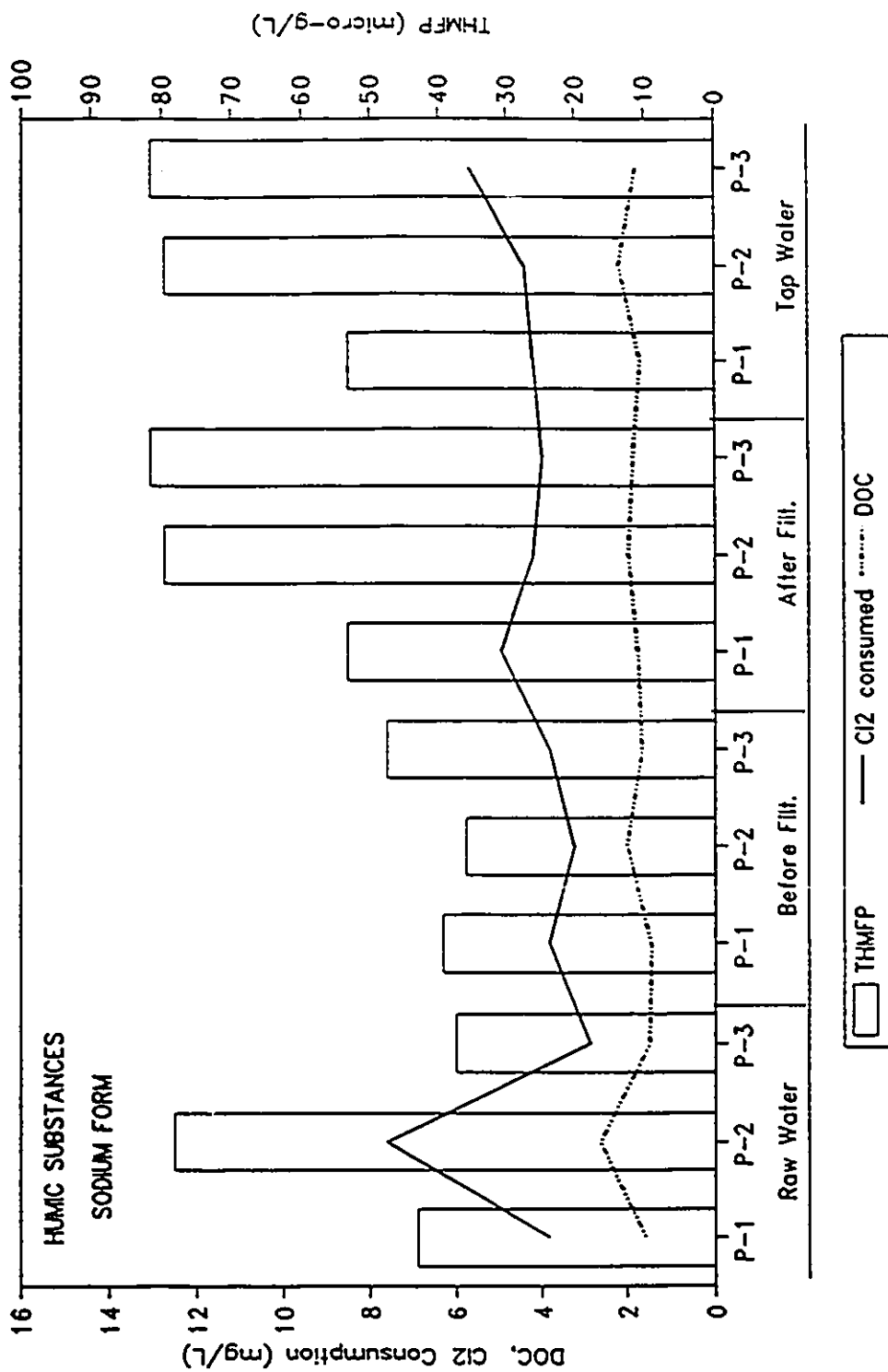


Figure 5.21. THMFP, DOC and chlorine consumption characterization of fractionated samples, April 1993 (sodium form).

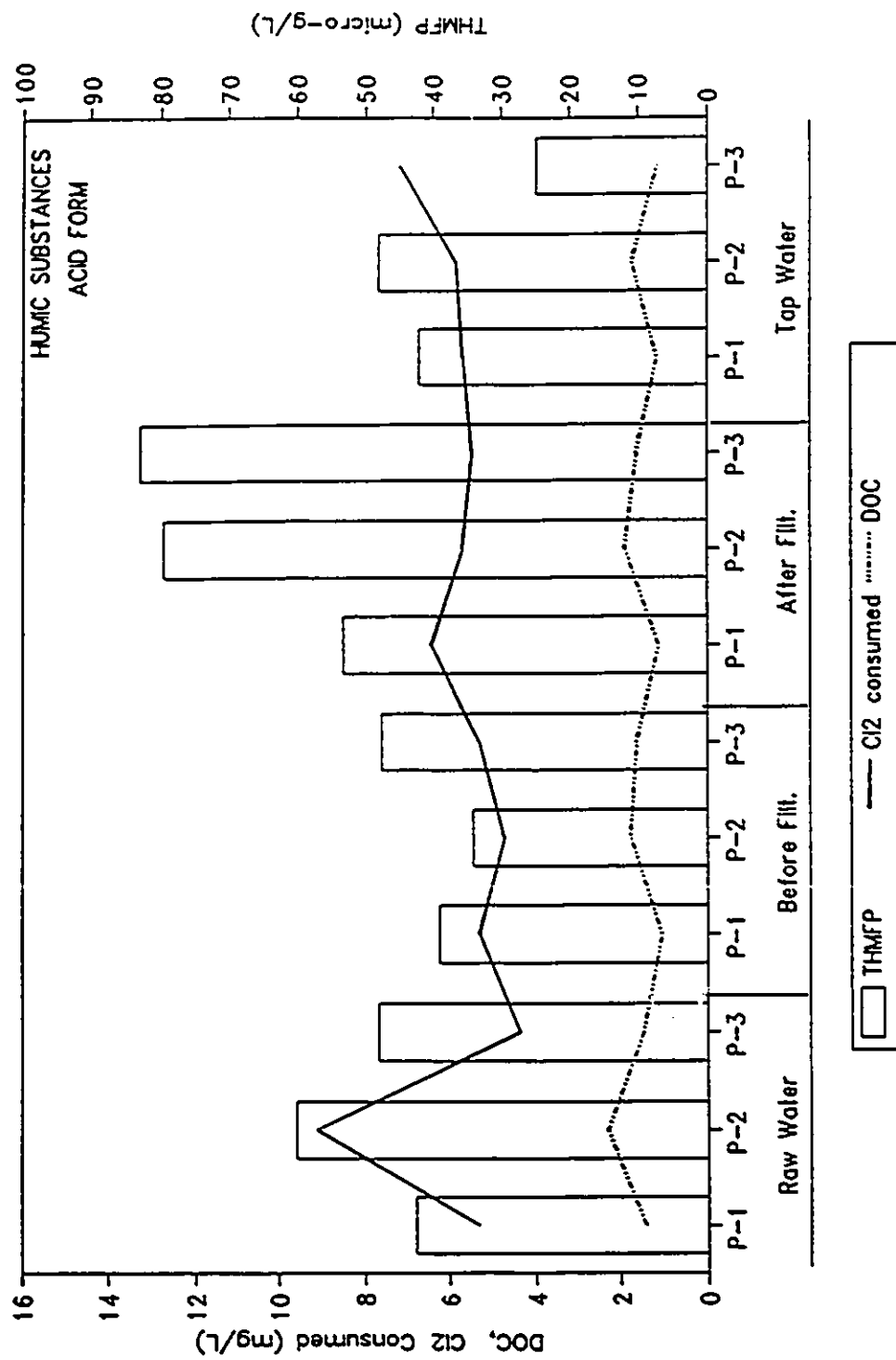


Figure 5.22. THMFP, DOC and chlorine consumption characterization of fractionated samples, April 1993 (acid form).

reaction was quenched with sodium sulphite. During this waiting period, the samples were preserved as recommended by Standard Methods, Method No. 5710 A (APHA-AWWA-WPCF, 1989). However, the recommended time limit for storage before analysis is 14 days. After this time, biodegradation of the sample is highly probable (USEPA, 1982).

5.1.6. AMSD by High Performance Size Exclusion

Chromatography

Since HPSEC offers certain advantages over GPC in the determination of AMSD, e.g., a reduction in the analysis time and a high precision in the flow rate control, samples for March 1993 and April 1993 were analyzed for AMSD by this method. Similarly to GPC, due to gel-solute interactions, elution behaviour of humic substances is highly dependent on eluent characteristics such as pH and ionic strength. Different kinds of eluents such as sodium hydrogen carbonate (NaHCO_3) and phosphate buffer (KH_2PO_4) were initially tried at various pHs and with different concentrations of the buffer. Once a linear response was obtained for the proteins used in the calibration for the determination of molecular size, the AMSD of the humic substances in both acid and base forms were determined.

Figures 5.23 to 5.26 present the AMSD chromatograms. As can be seen, the molecular size range obtained by this method was between 20,000 to 50,000, which is different in range from the AMSD chromatograms obtained in the GPC system (less than 3000 to more than 50,000). This was expected both due to the differences in column

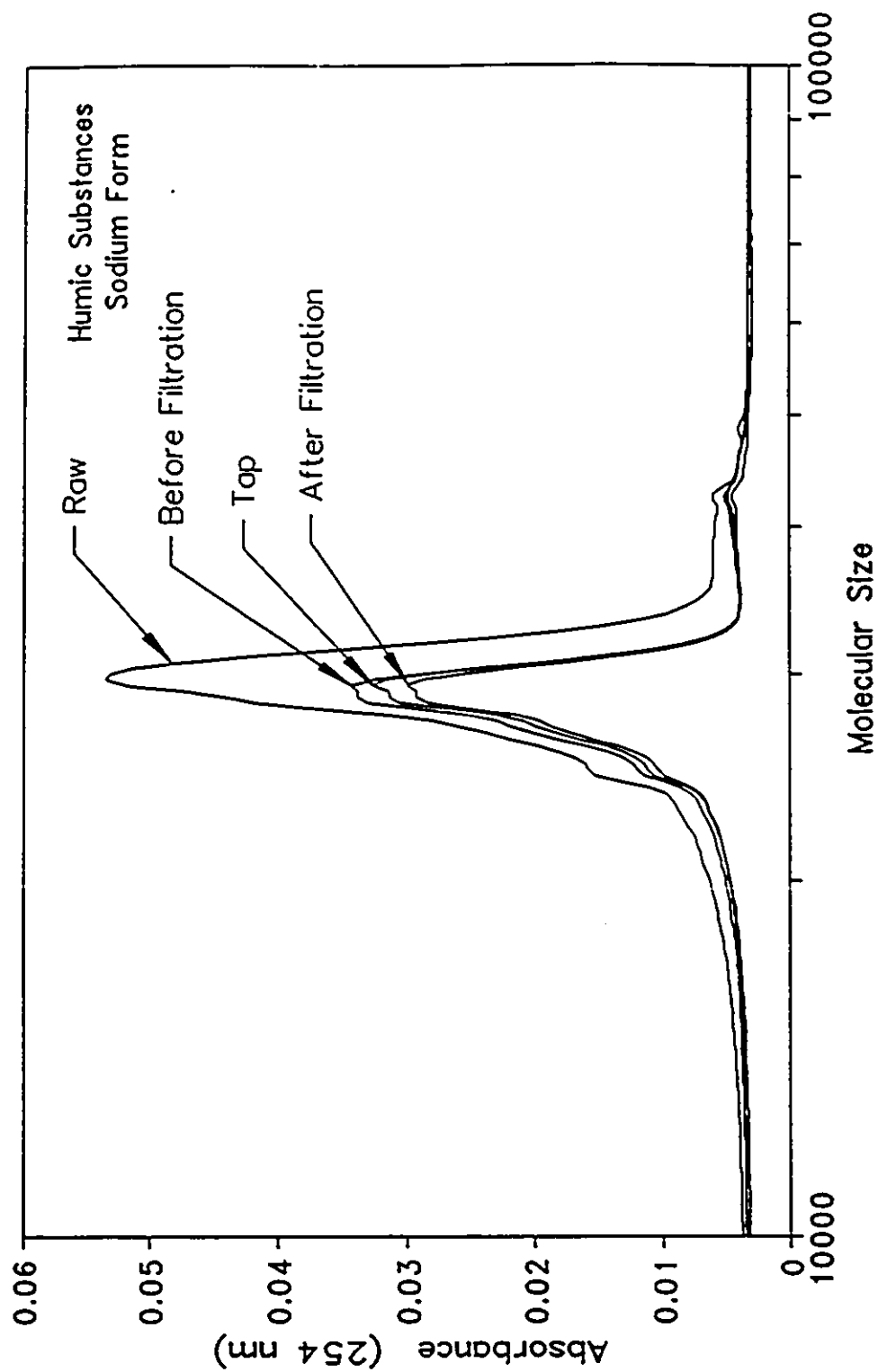


Figure 5.23. HPSEC-AMSD of humic substances, sodium form, March 1993.

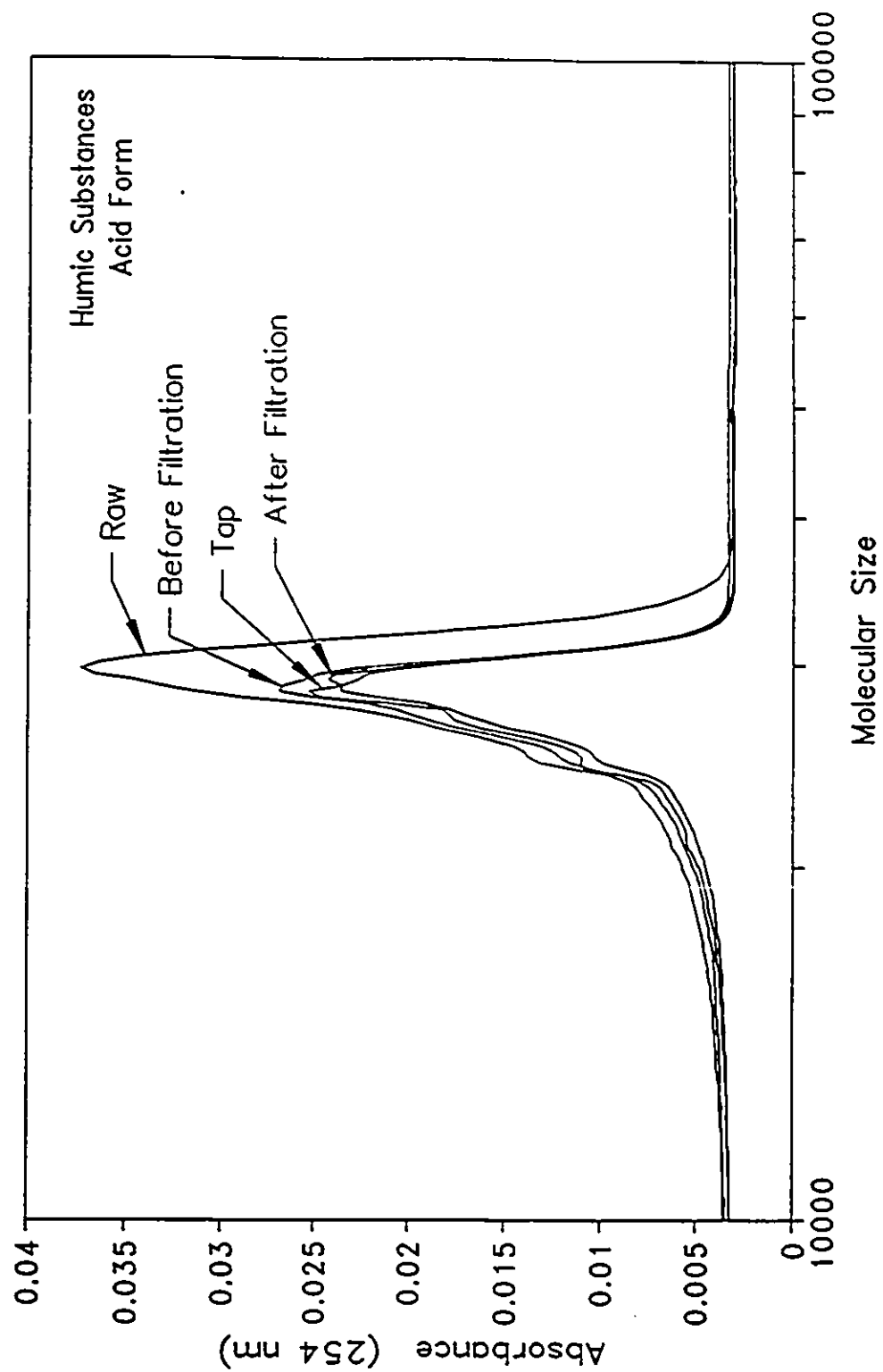


Figure 5.24. HPSEC-AMSD of humic substances, acid form, March 1993.

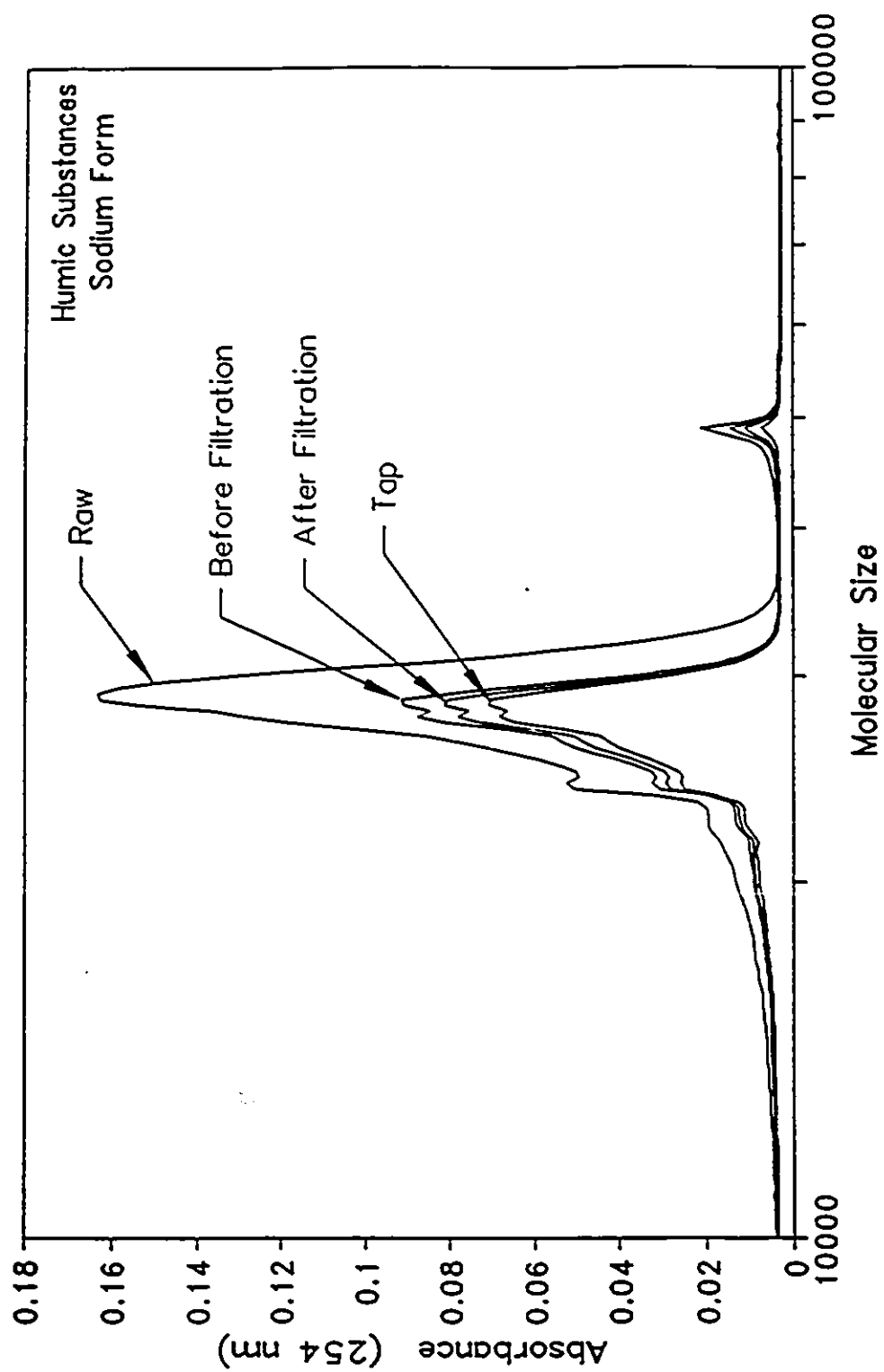


Figure 5.25. HPSEC-AMSD of humic substances, sodium form, April 1993.

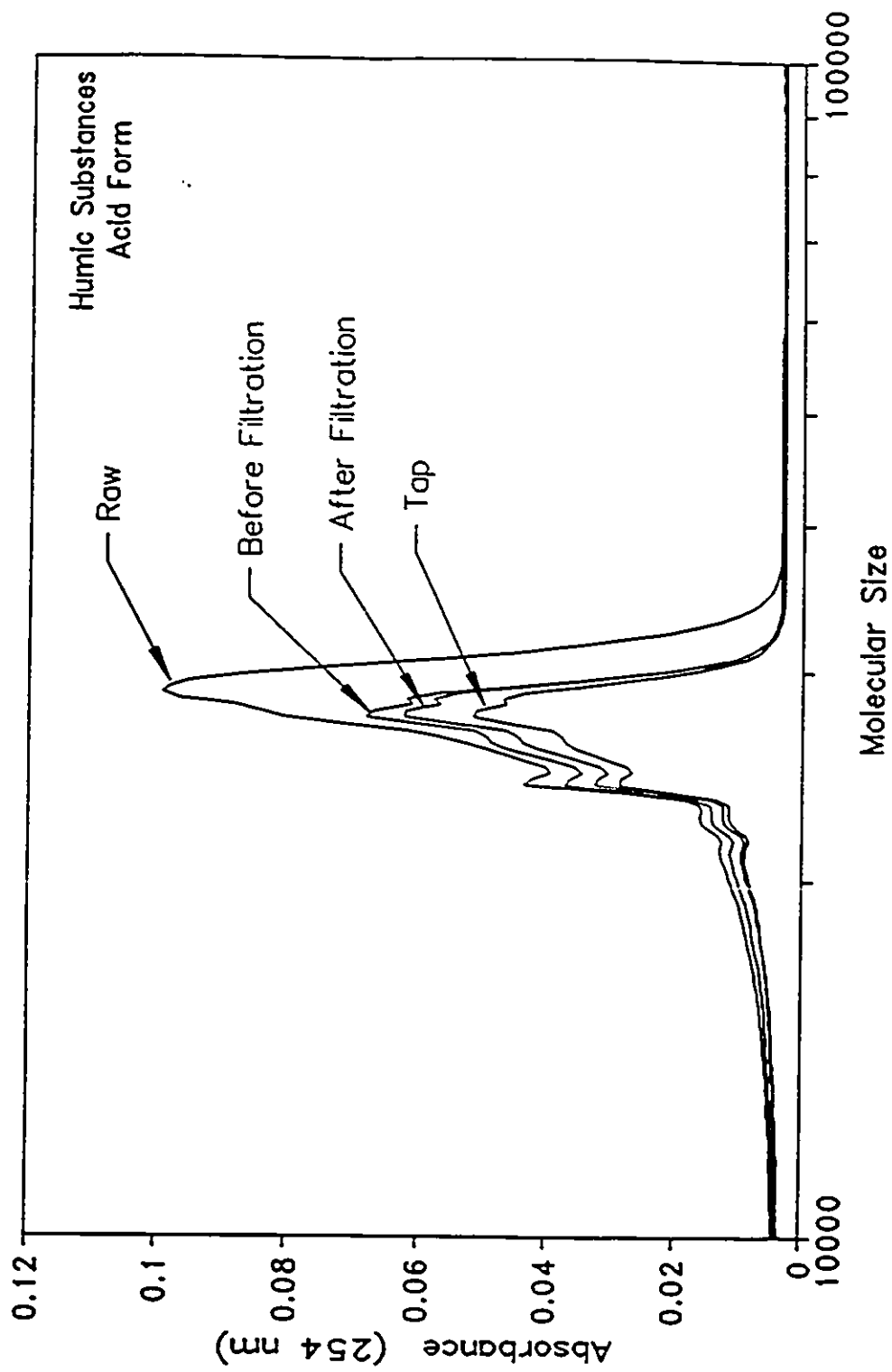


Figure 5.26. HPSEC-AMSD of humic substances, acid form, April 1993.

materials used for the two systems and due to the unknown chemical composition, behaviour and shape of the humic substances. Despite these differences, the distribution of the molecular size in these chromatograms shows roughly the same trend. The relative total area reduction between different samples is similar to the relative total area reduction obtained in the GPC system. This demonstrates that both systems can be used as a tool to measure the performance of the different processes in the removal of humic substances. However, the actual distribution of the molecular size components in the sample is undetermined because it is dependent on the system, the standards used in its calibration and the conditions used for its determination.

Only a few researchers have reported the application of HPSEC to humic substances (Gloor *et al.*, 1981; Becher *et al.*, 1985). The AMSDs of humic substances reported by Becher *et al.*, (1985) using a globular protein calibration curve are similar to those reported in this research. According to their study, the molecular size of the humic substances depends on the standards used for the calibration. By calculating the molecular size of the same humic substances, using the dextran "universal calibration curve" of Frigon *et al.*, (1983), it was found that these values compared well with the values reported in the literature by Glaze *et al.*, (1980). All these results suggest that dextrans, due to their coiled configurations, are more appropriate than globular proteins for the calibration of the HPSEC column. In this study, since the AMSD of humic substances was used mainly as a tool to determine their removal along different treatment processes, no attempt was made to use dextrans as a reference for the AMSD.

5.2. Separation of Humic / Fulvic Acids

The procedure used in this work to concentrate humic substances was an abbreviated version of a procedure developed by Thurman and Malcolm (1981) to extract humic and fulvic acids. The extract was further separated into fulvic and humic fractions by acidification until pH 1 and separation by centrifugation. The soluble fraction was fulvic acid and the residue was labelled as the humic fraction. Fulvic acid is characterized by a lower molecular size than humic acid. This additional separation step, humic/fulvic split, was performed in order to determine which molecular size fraction of the humic substances is more reactive in the formation of THMs and to determine the approximate content of the humic and fulvic fractions in the Detroit River water.

In this study, the humic and fulvic fractions were compared with those of the "standard humic substances" provided by the Humic Substances Society (McCarthy and Suffet, 1989). Results from these determinations are presented in the following sections.

5.2.1. Apparent Molecular Size Distribution

The AMSD of the standard humic and fulvic acids were determined using both the GPC and the HPSEC systems. Figures 5.27 to 5.30 show the UVA and the DOC chromatograms obtained by each system. As observed from the chromatograms for samples collected in March 1993 and April 1993, there is a difference in the range of molecular sizes determined by the two systems. However, the peaks observed by the GPC for the standard fulvic and humic acids, corresponding to molecular size values of 5,000 and 20,000 respectively, are within the molecular size range observed for the

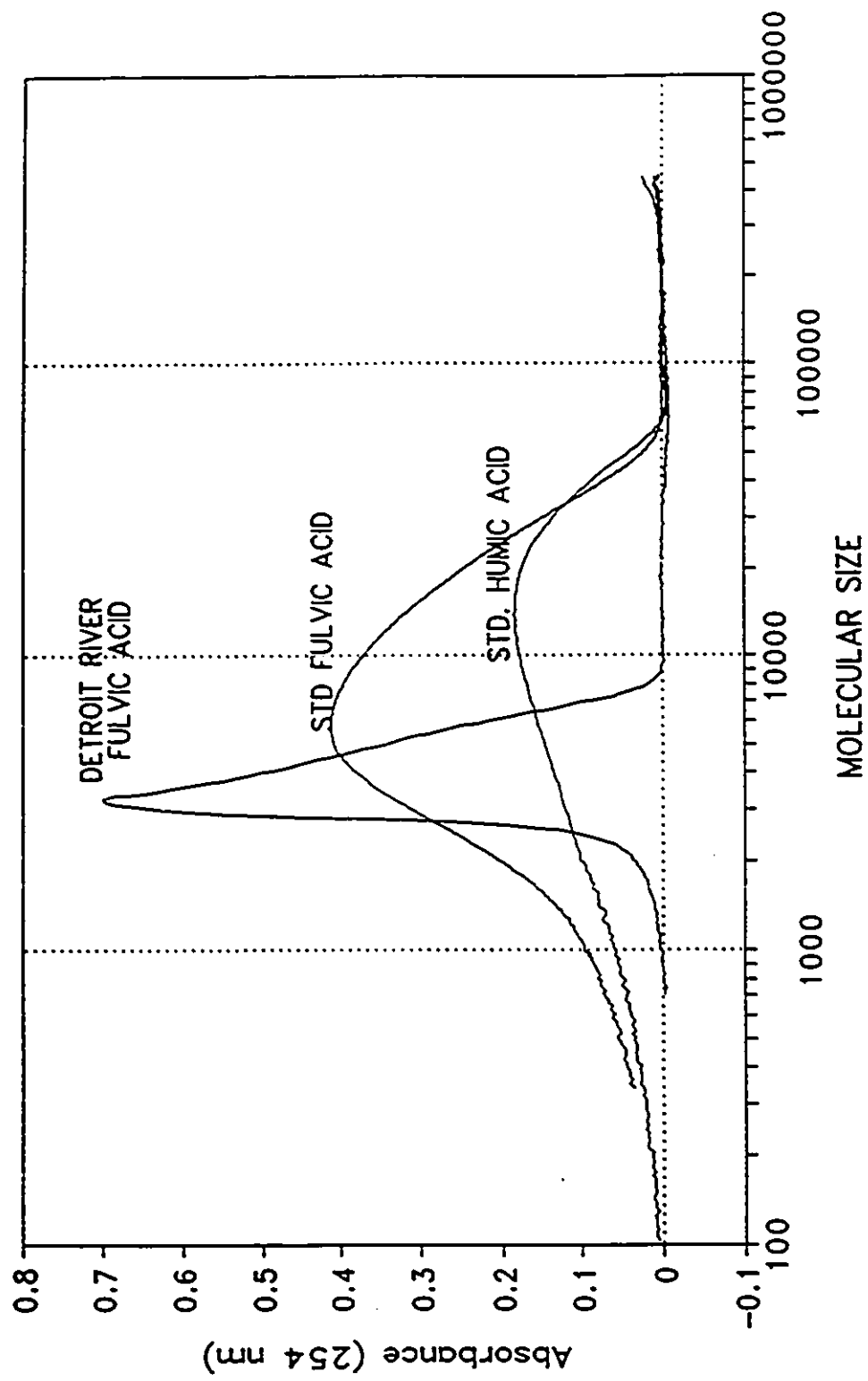


Figure 5.27. UVA-AMSD of standards and sample (April 1993).GPC

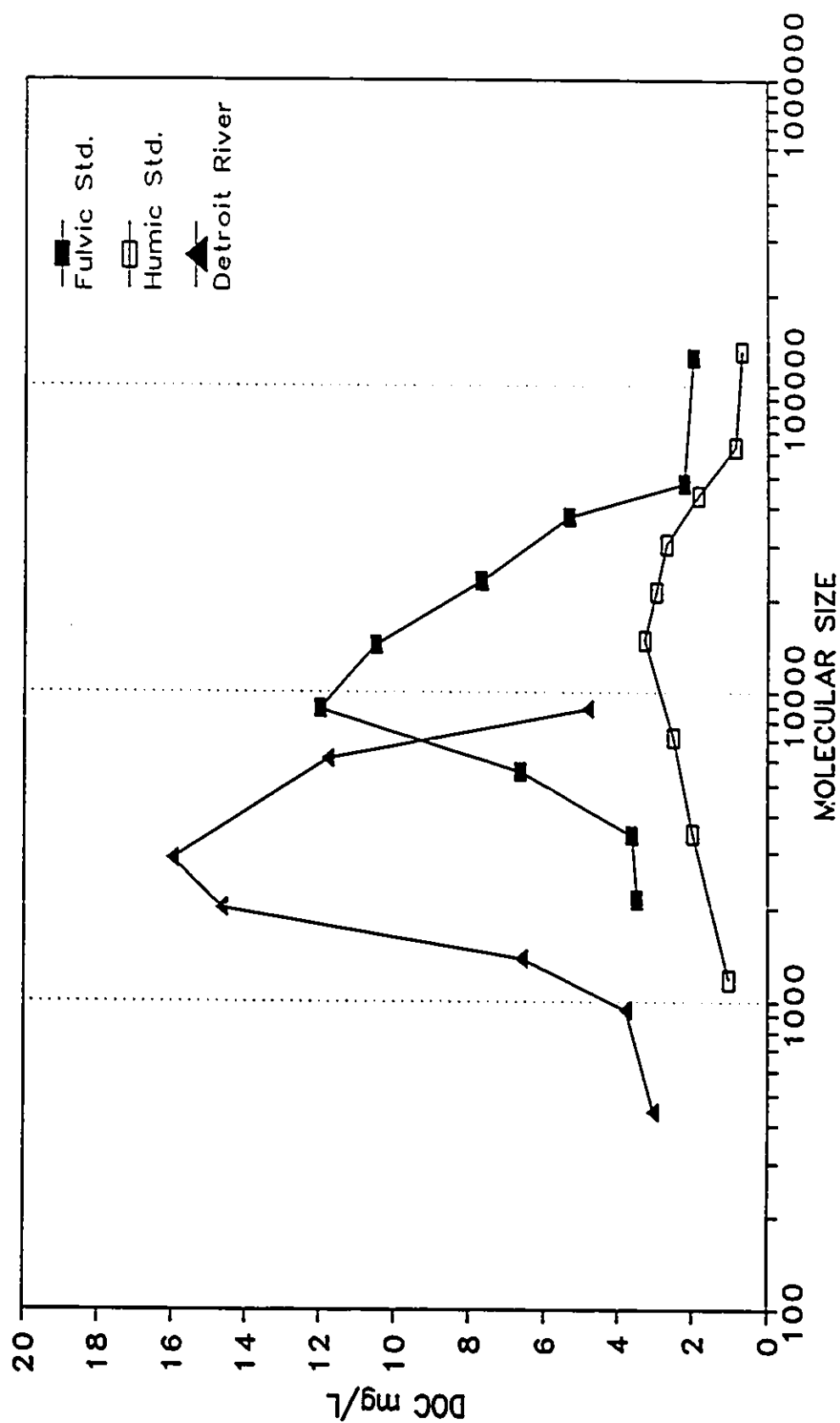


Figure 5.28. DOC-AMSD of standards and fulvic acid sample (April 1993)-GPC

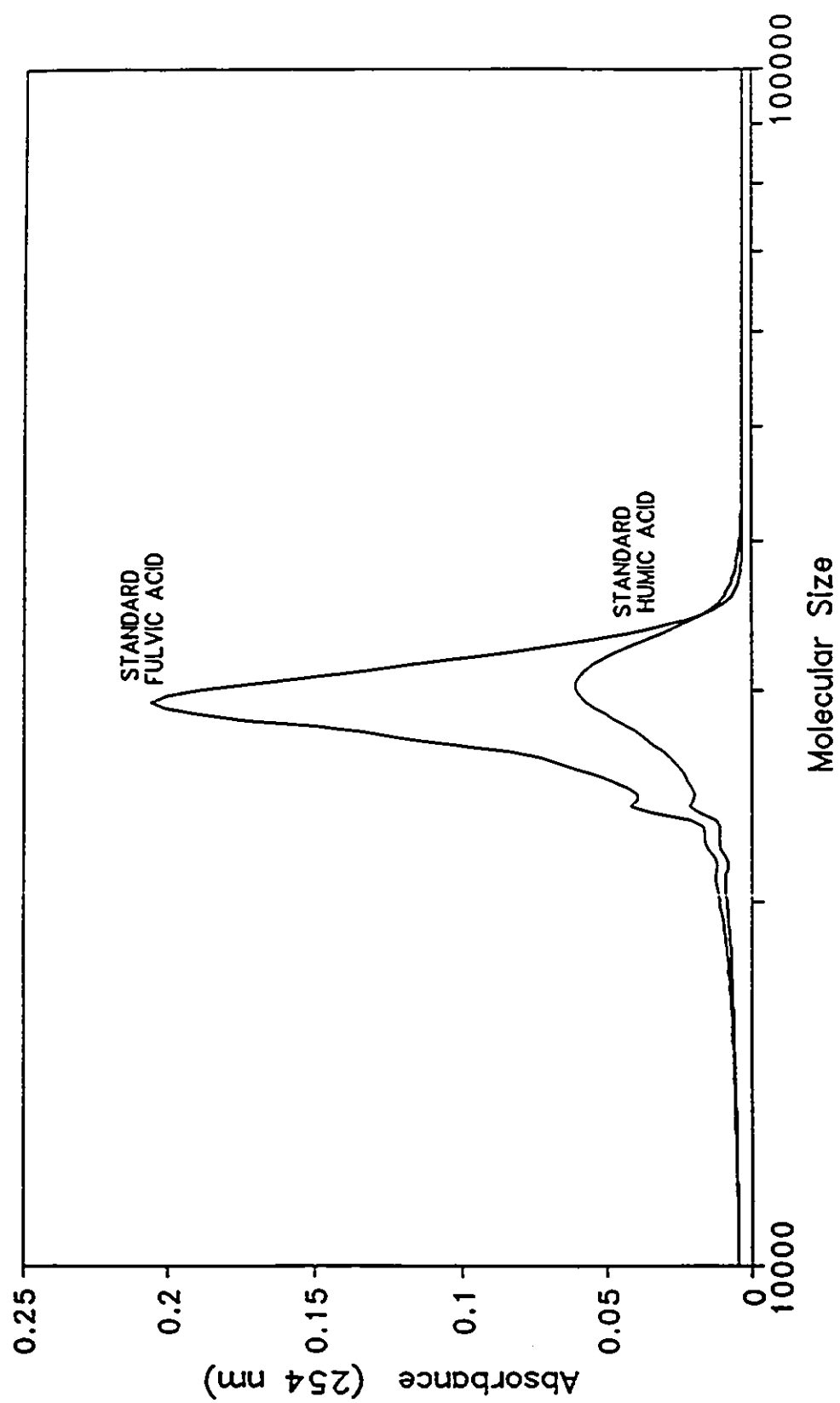


Figure 5.29. UVA-AMSD of fulvic and humic acid standards-HPSEC

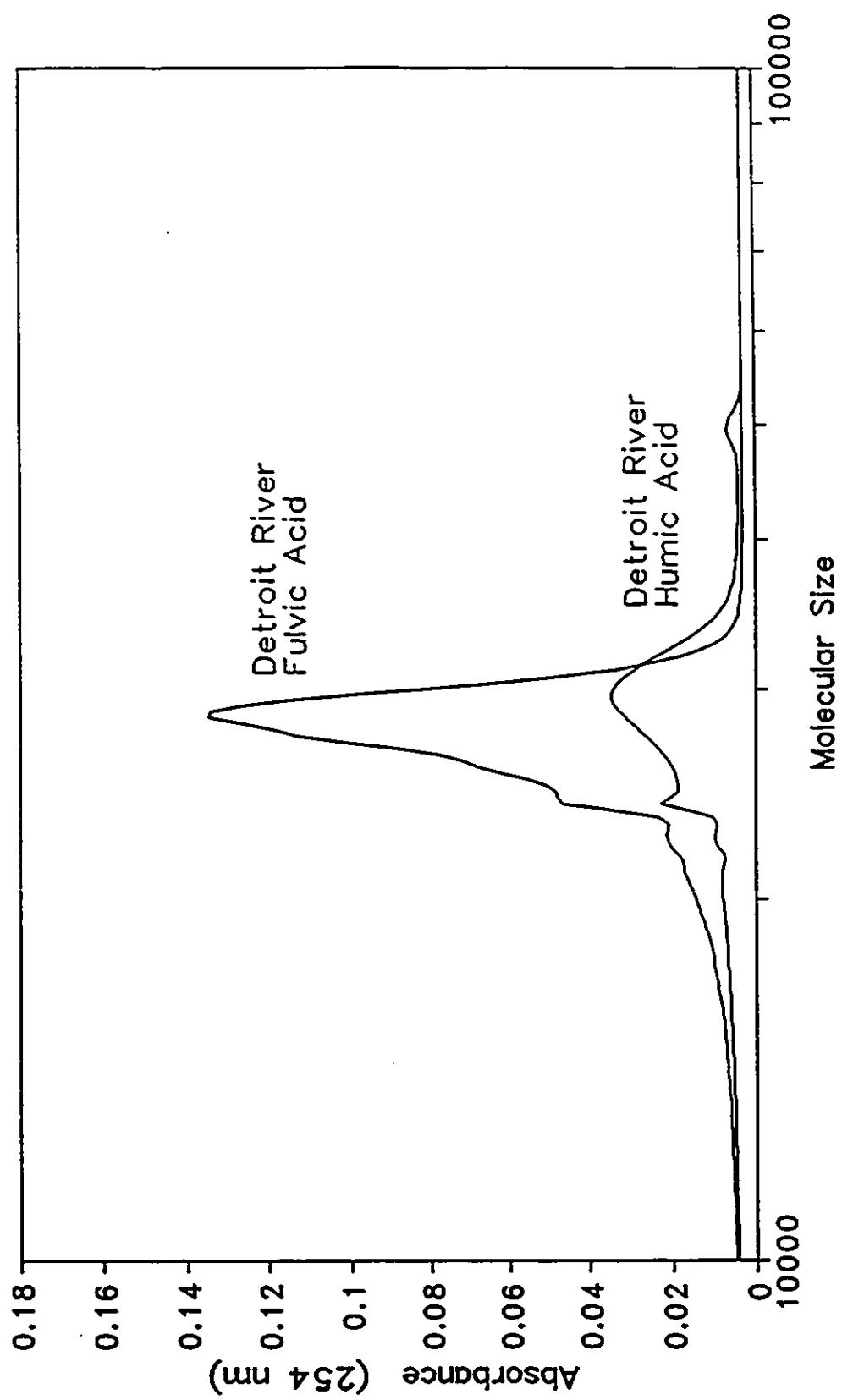


Figure 5.30. UVA-AMSD of fulvic and humic acid (April 1993 sample)-HPSEC

humic substances previously analyzed in this research. The AMSD of the fulvic acid obtained for the April 1993 sample is illustrated in the same chromatogram and shows a peak at the molecular size of 3,000. The two fulvic acids are different in molecular size, as expected, since humic substances are characterized by geographical location. However, these values are close and within the ranges reported in the literature for GPC molecular size determinations. Due to sample limitations, it was not possible to analyze the humic acid of the April sample using GPC. In addition to the UVA-AMSD determination, the DOC-AMSD relationship was also determined for the GPC system and the results are presented in Figure 5.28.

The HPSE chromatograms of the standards and the samples show that there are no significant differences in the molecular size for both the humic and fulvic acid standards and the samples. In this system, the molecular size of the fulvic acid was 28,000 and the molecular size of the standard was 29,000. For the humic acid, the molecular size of both the standard and the sample were the same, 30,000. A small peak was observed in the high molecular size of 50,000 for the humic acid sample. This peak could be associated with the peak detected previously in the April 1993 sample. The reason that this appears only in the sodium form and not in the acid form can be attributed to the fact that humic acid is insoluble at low pH and that part of these had probably been retained in the ion exchange column during the analytical procedure used to obtain the acid form of humic substances. The molecular size of the fulvic acid, 28,000, agrees with the molecular size from the peaks obtained previously in the AMSD of humic substances for the March and April 1993 samples.

5.2.2. THM Reactivity of Fulvic and Humic Fractions

Various concentrations of the standard fulvic and humic acids were prepared in order to determine the correlation between the DOC and the UVA. Results are presented in Figure 5.31. It is observed from these plots that humic acid has a higher UVA for the same DOC concentration.

From the DOC concentration and the volume of the two fractions obtained after the humic/fulvic split, the relative content of fulvic to humic acids was determined to be 94 percent fulvic acid and 6 percent humic acid. This agrees with the distribution of humic substances in natural waters reported by Thurman (1985).

In order to determine the THMFP of the standard humic and fulvic acids, solutions with three different concentrations of DOC (9, 2 and 1 mg/L) were chlorinated with a dosage of 10 mg/L of chlorine. The chlorine consumption from these solutions and the THMs formed were determined with respect to time at 0.2, 1, 2, 4 and 7 days. It was observed that after 4 hours, all the chlorine was consumed in the solution containing 9 mg/L of DOC. Results are presented in Figures 5.32 and 5.33 for 2 and 1 mg/L solutions respectively. As shown in these plots humic acid has a higher chlorine consumption and a higher THMFP yield than fulvic acid for the same chlorine dosage and DOC concentration. The observation that humic acid fractions have higher THM reactivity than their corresponding fulvic acid has also been reported by other researchers (Oliver and Thurman, 1981 and Reckhow *et al.*, 1990).

The THMFPs of the fulvic and humic acid samples were determined only after seven days and these gave a reactivity of 25 and 40 $\mu\text{g THM/mg C}$, respectively. This

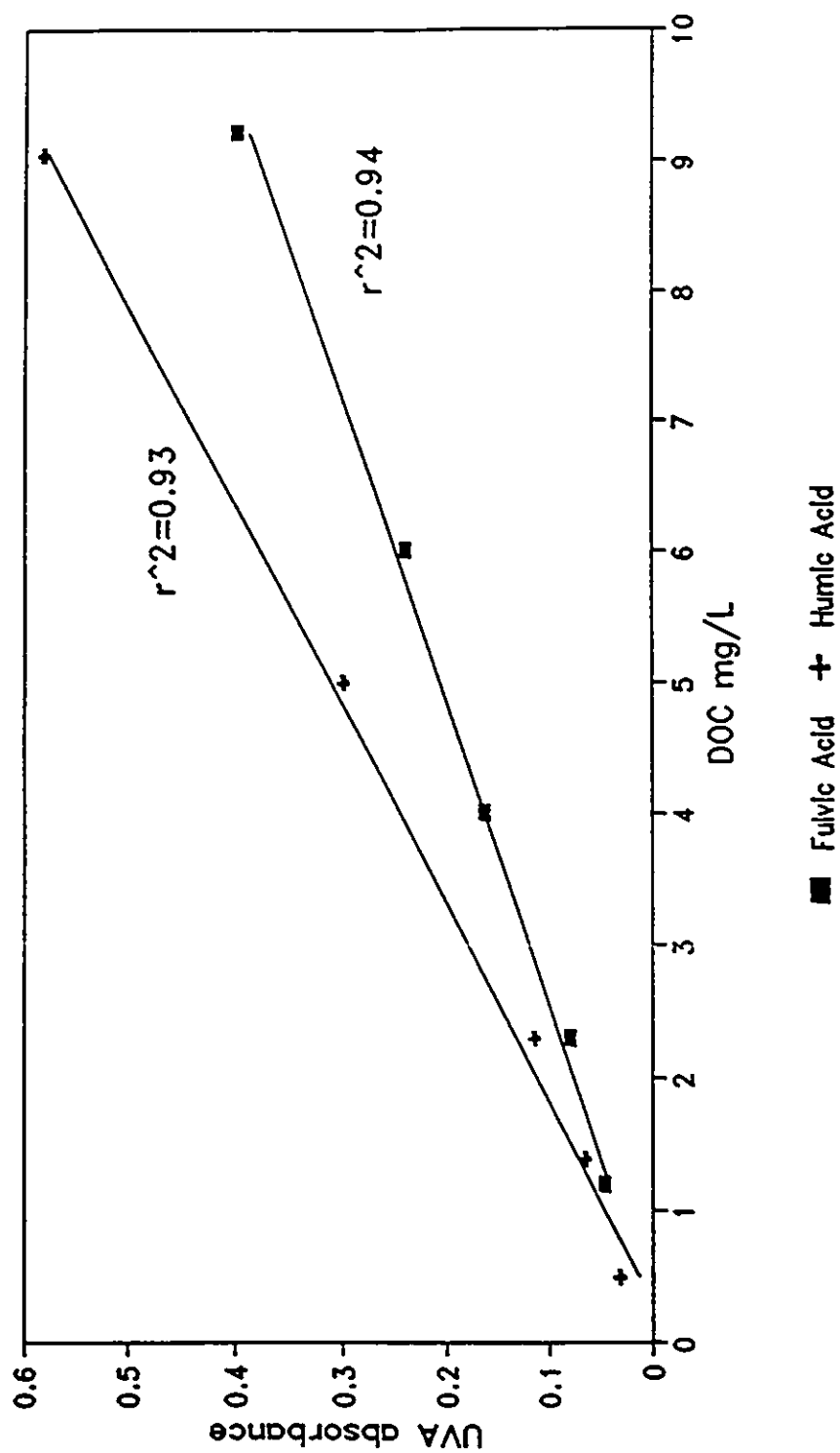


Figure 5.31. UVA vs. DOC correlations for fulvic and humic acid standards

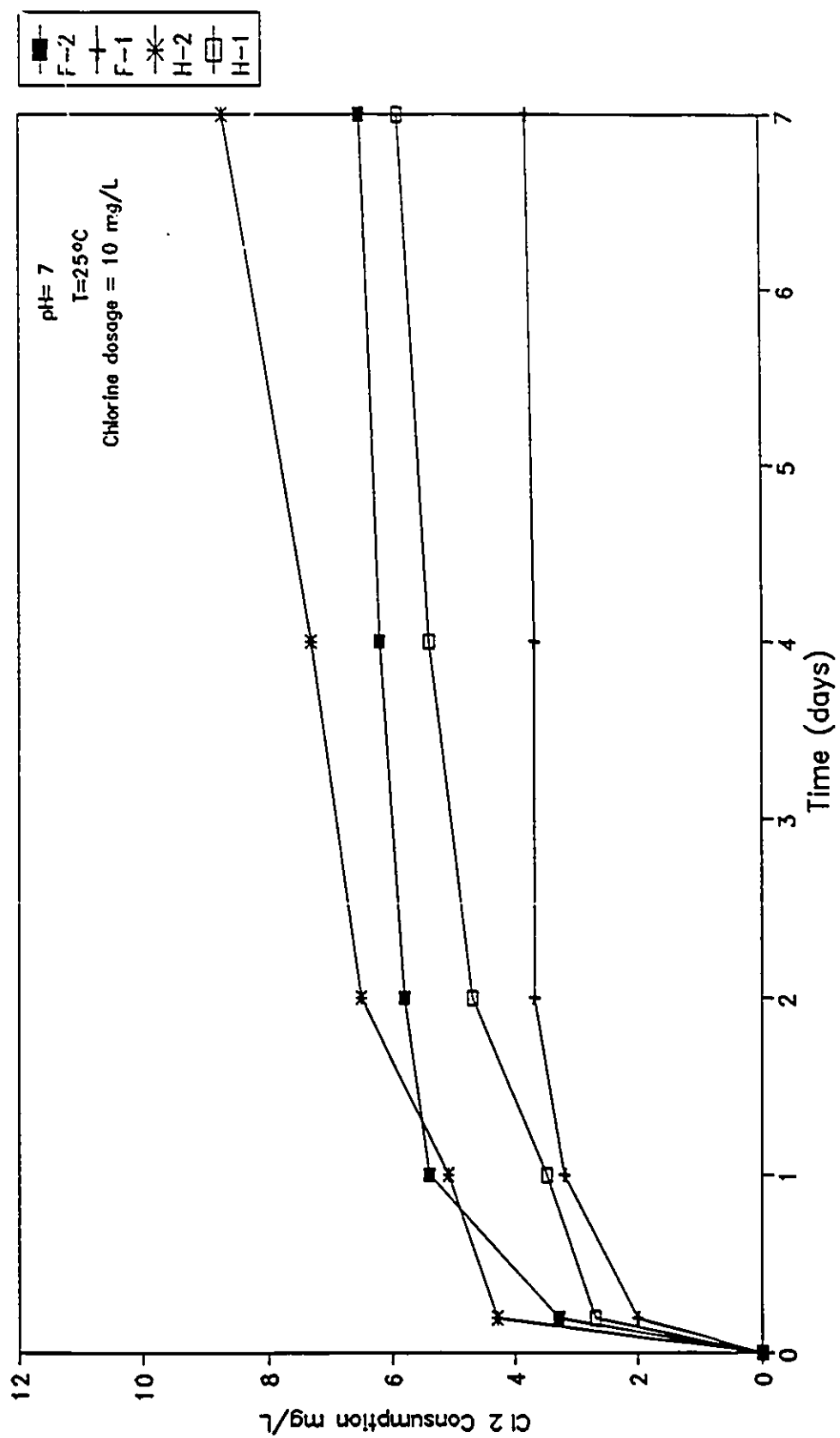


Figure S.32. Chlorine consumption by humic and fulvic acid standards

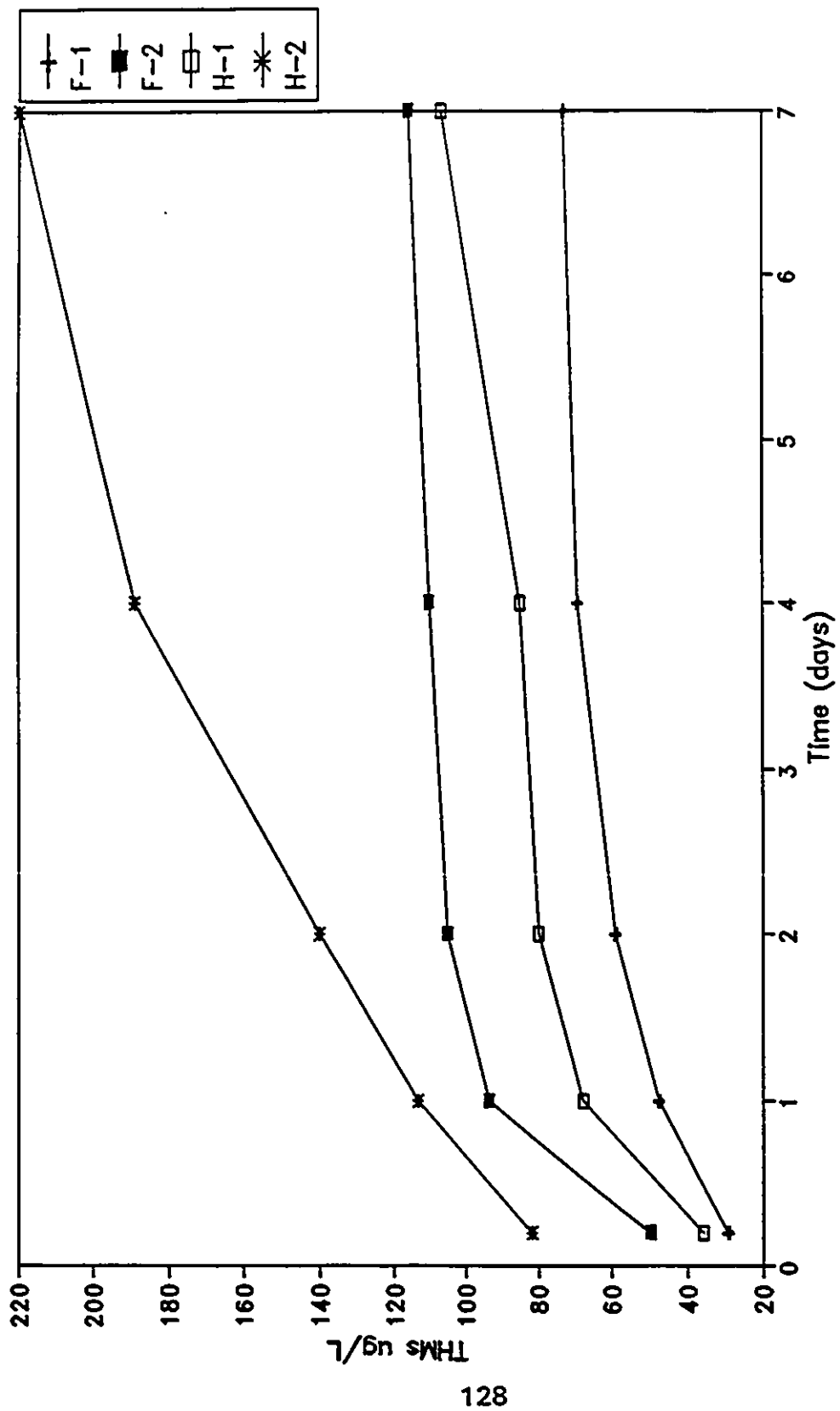


Figure 5.33. THMFP of humic and fulvic acid standards.

corroborates the findings that humic acid, characterized by a higher molecular size than fulvic acid, has the higher THM reactivity. The comparison of these reactivities of the samples with that of the standards, 55 and 86 $\mu\text{g THM/mg C}$, indicates that the samples had lower reactivities. This indicates that the humic and the fulvic acids from the Detroit River water have a lower reactivity than the fulvic and the humic acids from the Suwannee River (Southeastern Georgia, USA) that were used to prepare the "standard fulvic and humic acids". This was expected because the Suwannee River originates in a swamp located in a southern temperate zone that is characterized by a high content of humic substances, colour and DOC. According to other researchers (Peters *et al.*, 1980; Oliver and Thurman 1981; Miller and Uden, 1983), there are wide variations in THM reactivities for humic materials from diverse climatic and geological environments. These variations are attributed to the differences in chemical and functional group composition of aquatic humic substances from source to source. The humics present in ground waters had the lowest THM reactivities, marsh-bog humics had the highest THM reactivities and surface water humics had intermediate THM reactivities (Oliver and Thurman, 1981). Determination of other characteristics of these humic substances, such as elemental composition, functional group analysis and TOX will be necessary to more fully analyze the influence of source characteristics on THM reactivities.

Chapter VI

RESULTS AND DISCUSSION OF PILOT PLANT STUDIES

6.1. General

As noted in the previous chapter, conventional treatment processes can reduce the concentration of humic substances, and consequently decrease the THMFP of the treated water. However, further improvement in the water quality will require either: *i)* a modification in the actual process, or *ii)* utilization of advanced processes. Both alternatives must be analyzed first in a pilot plant in order to evaluate their applicability and viability. The second option was selected for pilot plant assessment by the MOEE and the WUC. This pilot plant started operation in January 1993 and only by October 1993 were stable conditions obtained, hence only one set of samples was collected and analyzed.

The results presented in this chapter provide the removal efficiency of humic substances in the pilot plant equipped with two parallel trains of treatment: *i)* conventional treatment using, in addition, GAC, *ii)* conventional treatment with ozone after filtration and GAC.

Samples from the untreated and treated water after each process were taken and analyzed utilizing the general procedures described in Chapters III and IV.

6.2. General Characterization

A summary of the results of the characterization of the untreated and treated samples is presented in Table 6.1. A temperature increase was detected in both treatment trains and higher temperatures were detected in the ozone train. The pH decreased along both treatment processes, with a greater decrease for the chlorine train. Turbidity, DOC and UV absorption were significantly reduced in all cases. The DOC was greatly reduced after the GAC process. No THM(ins) were detected in the ozone train, since the bromide concentration in this water was below detection limits and the ozone dose applied was relatively low compared to the usual higher ozone dosage used for oxidation purposes. In the chlorine line, the THM(ins) concentrations formed after prechlorination were comparable with the values obtained from the WWTP for the months of March and April 1993. After GAC, no THM(ins) were detected. This confirms the statements in the literature that GAC is able to remove THM precursors and THMs (Lykins *et al.*, 1987; Weber and Bernardin, 1987).

6.3. Removal of DOC and Humic Substances

A summary of the removal behaviour of DOC and humic substances, observed after each process at the pilot plant is presented in Table 6.2. There are reductions in both DOC and humic substances concentrations in both treatment trains. Figure 6.1 shows comparatively the reduction of humic substances after each process along the two trains. A total reduction of 55 percent is achieved by conventional treatment in the

Table 6.1. Results of October 6, 1993 sample characterization at the pilot plant.

SAMPLE	Temp °C	pH	Turb	Alk mg/L as CaCO ₃	DOC mg/L	UVA 254 nm	Cl ₂ mg/L	Residual Cl ₂ mg/L	TU1M (Inst) mg/L
C h l o r i n e	Raw	13.4	7.74	5.48	82.3	2.00	0.024		
	Coag-Sedim	13.5	7.27	2.34	78.3	1.75	0.011	1.5	25
	Filtration	13.7	7.27	0.07		1.58	0.007	1.11	26
	GAC	14.1	7.17	0.07		0.63	0.005		
O z o n e								O ₃ mg/L	
	Raw	13.4	7.74	5.48	82.3	2.00	0.024		
	Coag-Sedim	14.9	7.26	1.36	77.02	1.71	0.018		
	Ozone Dissipation					1.65	0.008	*	0.05
	Filtration	16.5	7.24	0.05		1.60	0.008		
	GAC	17.4	7.39	0.08		0.62	0.002		

* Ozone concentration in the contact chamber = 0.1 mg/L; transfer efficiency = 86%

Table 6.2. Removal behaviour of DOC and humic substance concentrations at the pilot plant.

	Sample DOC mg/L	Non-Humic DOC mg/L	Humic Substances mg/L	% Reduction		
				Non-Humic	Humic Substances	DOC
C h l o r i n e	Raw	1.50	1.05			
	Coag-Sedim	1.35	0.65	10	38	12.5
	Filtration	1.39	0.47	7	55	21
	GAC	0.61	0.05	60	95	70
O z o n e	Raw	1.50	1.05			
	Coag-Sedim	1.32	0.75	12	29	14
	Disinfection	1.46	0.51	2.7	52	17
	Filtration	1.38	0.48	8	55	20
	GAC	0.61	0.03	60	97	70

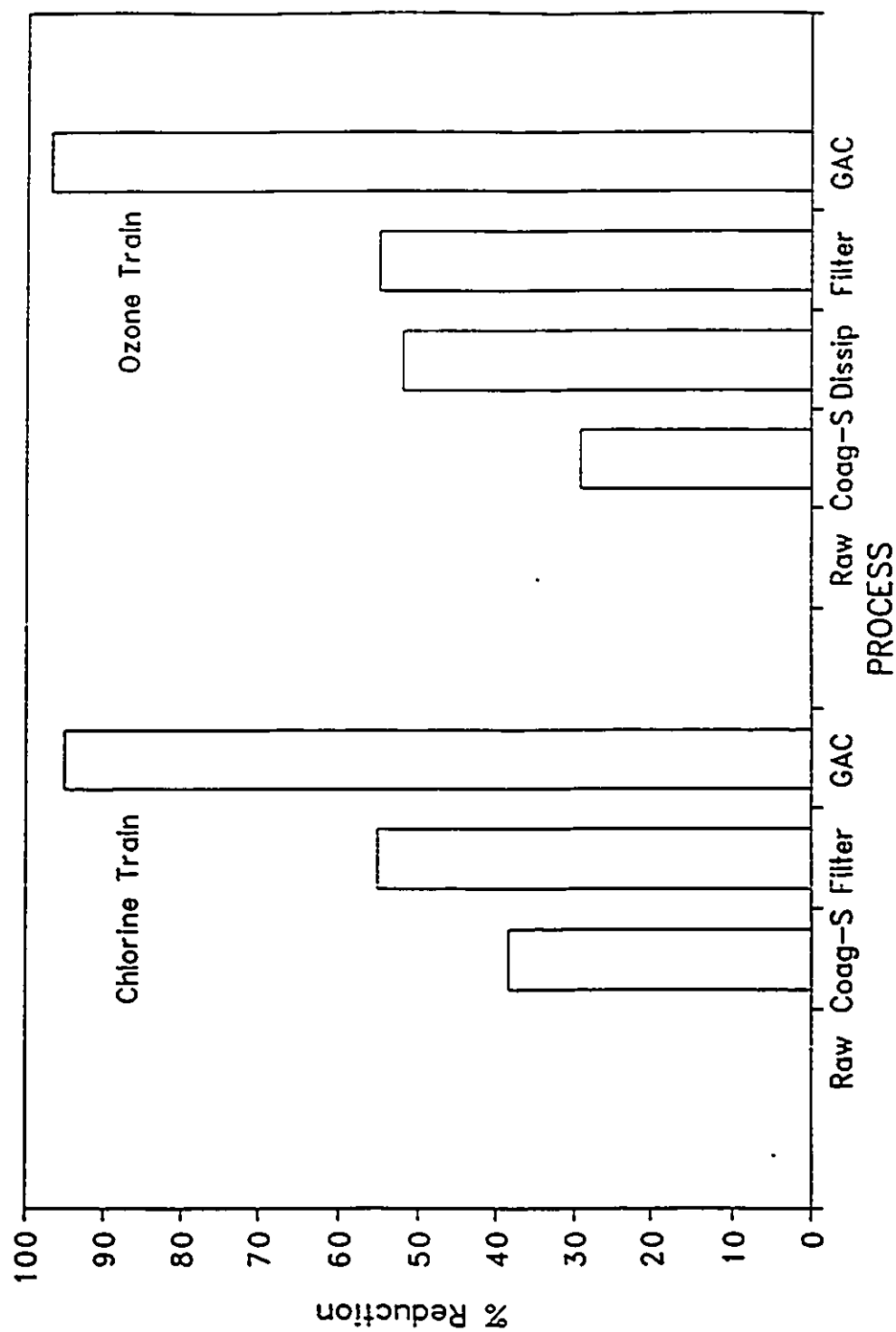


Figure 6.1. Humic substances reduction by different treatment processes.

chlorine train. Of this total, 38 percent was removed by both prechlorination and coagulation-sedimentation processes, and 17 percent was removed by filtration (anthracite/sand). In the ozone train, the same total reduction of 55 percent was observed, although only 29 percent was removed by coagulation-sedimentation. After ozonation in the dissipation chamber, the removal of humic substances increased by 23 percent. After filtration, an additional 3 percent was removed, which indicates that both oxidants, ozone and chlorine, have been effective in removing organic matter by altering the chemical composition of the humic substances, as reported in the literature (Glaze, 1987; Singer and Chang, 1989).

In the chlorine train, the coagulation-sedimentation process had a higher removal efficiency than in the ozone train. This was due to the fact that in the ozone train, ozone was added after coagulation-sedimentation rather than before as in the chlorine train. The effect of ozone as an oxidant was observed in the sample from the dissipation chamber, where 23 percent of the humic substances present before the ozonation, were reduced. It is probable that this removal was caused by the alteration of chemical properties of the humic substances to make them more adsorbable onto the colloid particles, which were removed during the laboratory filtration (0.45μ) procedure for humic substances analysis. Only a slight decrease in the humic substances in the ozone train during the filtration process was observed. This can be attributed to the various filtration mechanisms since the average particle diameter removed by anthracite and sand filtration is only about 2 microns and humic substances are comprised of particles smaller than

0.45 microns in diameter. Therefore, filtration could not be effective in removing humic substances, but it is a critical process for the removal of colloids and other particles.

The additional removal of humic substances by granular activated carbon was 40 percent for the chlorine line and 42 percent for the ozone line. Figure 6.2 indicates that the GAC is a very effective process in the removal of not only humic substances, but also of a large fraction of the non-humic substances (hydrophilic acids, carboxylic acids, amino acids, carbohydrates and hydrocarbons) which may not be removed in the conventional treatment system. It is important to point out that the GAC system, at the time of this sampling was in the second week of full operation and data on the time of breakthrough were not available.

6.4. Apparent Molecular Size Distribution

Since the AMSD provides a means of monitoring process performance and also provides information about the effects of the different processes on the molecular size distribution, the GPC and the HPSEC methods were used in this research to determine the AMSD after each treatment process. It is recognized that different methods provide different results. However, both methods were used, because concentrations of the humic substances isolated from the GAC sample were very low and could not be analyzed by the GPC and information was needed to compare these AMSD chromatograms with those obtained from the conventional processes at the WWTP.

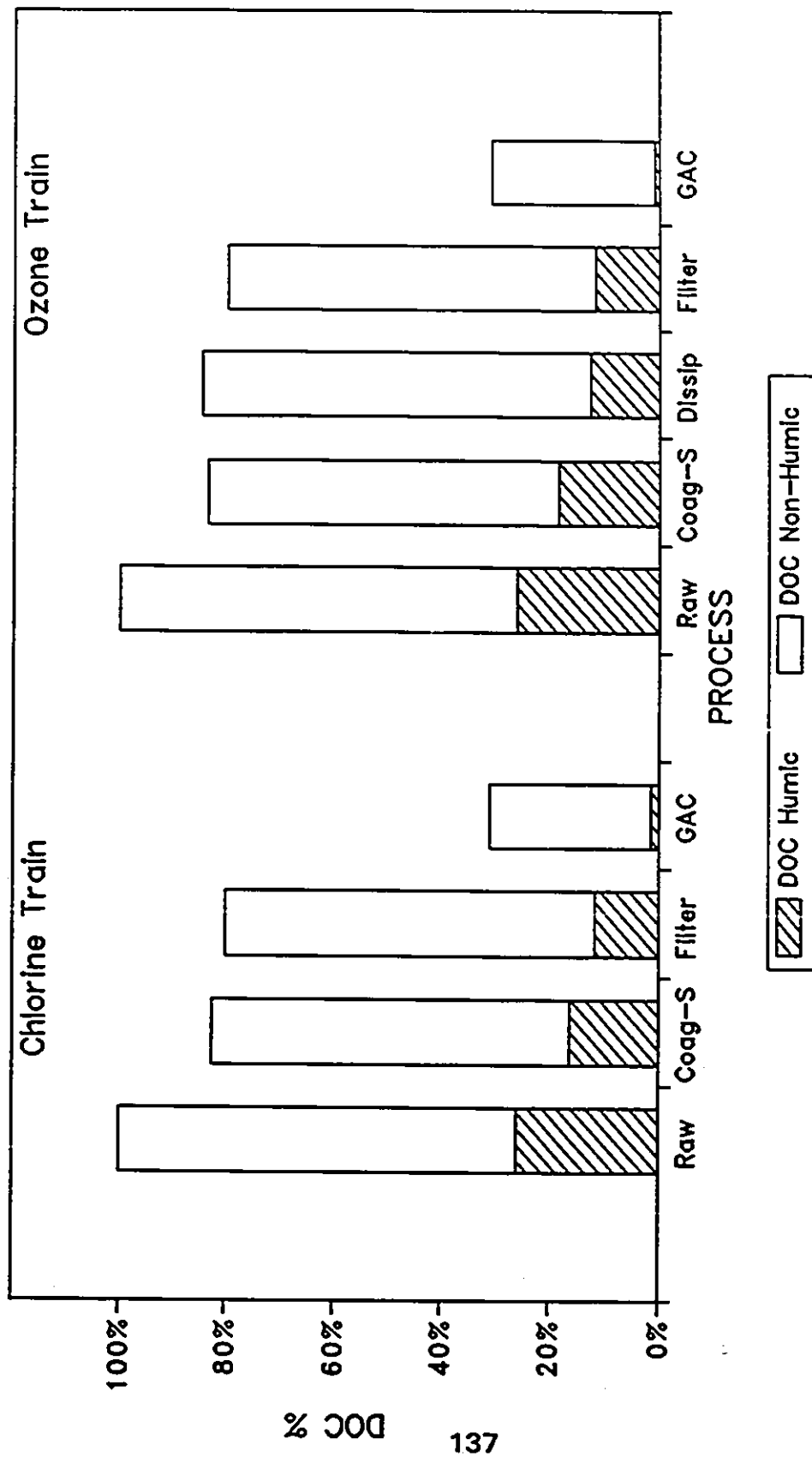


Figure 6.2. DOC reduction by different processes.

6.4.1. Gel Permeation Chromatography

Figure 6.3 presents the AMSD chromatograms for the chlorine train. The raw water chromatogram shows the three characteristic peaks from the Detroit River water, in the same molecular ranges as obtained in the WWTP. After coagulation-sedimentation, a total reduction of 40 percent was achieved, which is comparable with 37 percent removal obtained in the conventional treatment process at the WWTP. After filtration, an additional 6 percent removal was detected.

The AMSD chromatograms for the ozone train are presented in Figure 6.4. It was observed that essentially the same behaviour was obtained until after the coagulation-sedimentation process. After ozonation, a completely different chromatogram was obtained. Generally, there was a substantial reduction in all the peaks and a notable shift to the lower molecular size. After filtration, the AMSD was practically the same as the dissipation-sample chromatogram, but an increase in the high molecular size peak was detected. The chromatogram of the sample after filtration shows fewer peaks, which indicates that the organic matter had become less reactive.

6.4.2. High Performance Size Exclusion Chromatography

Figures 6.5 to 6.8 present the AMSD chromatograms obtained for the samples collected after different processes in each treatment train. In all these chromatograms, the reduction in humic substances after coagulation-sedimentation processes did not affect the molecular size distribution. This confirms the observations reported by Amy *et al.*, (1992). The humic substances were removed apparently intact by these processes and this

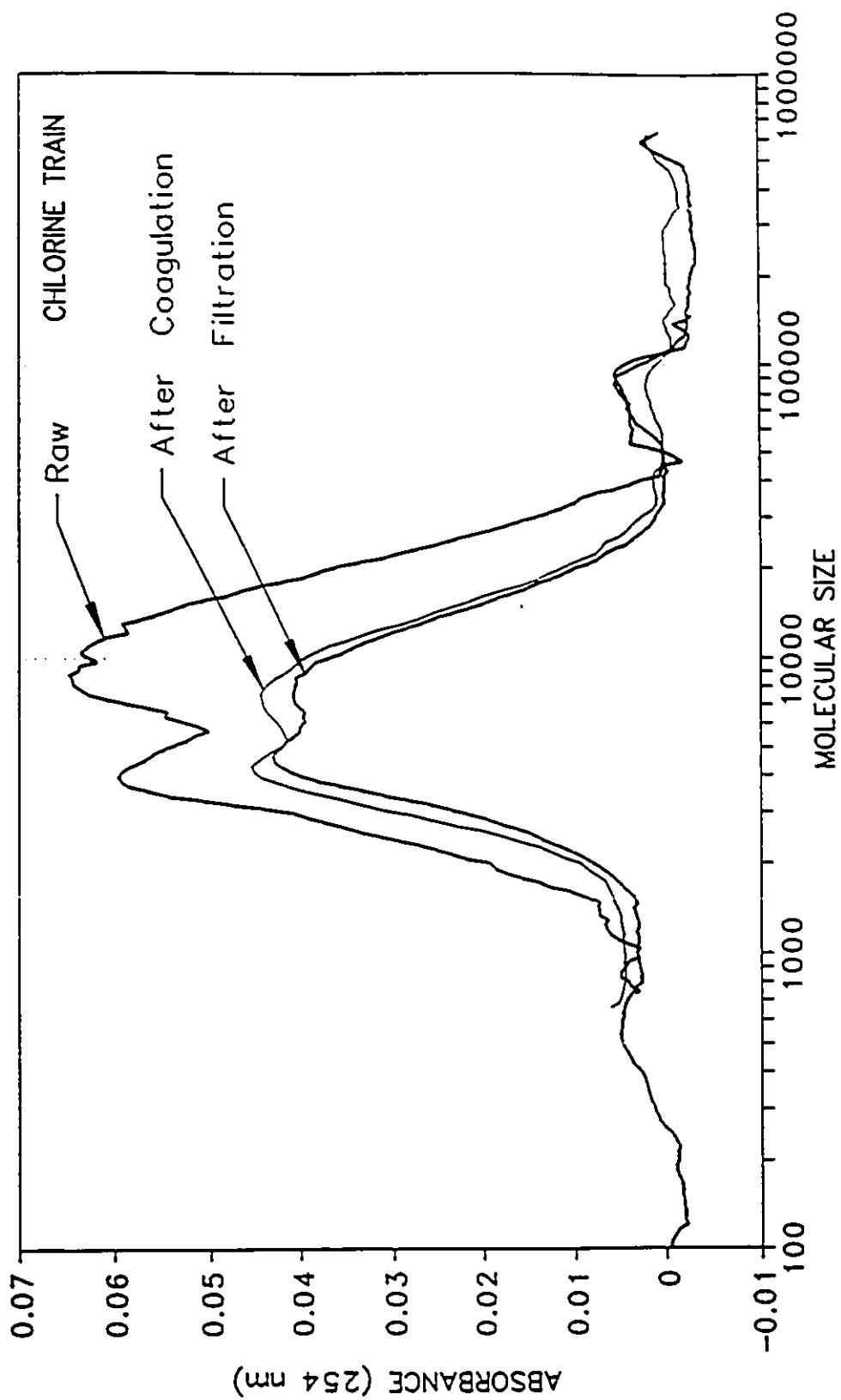


Figure 6.3. GPC-AMSD, of humic substances, chlorine train.

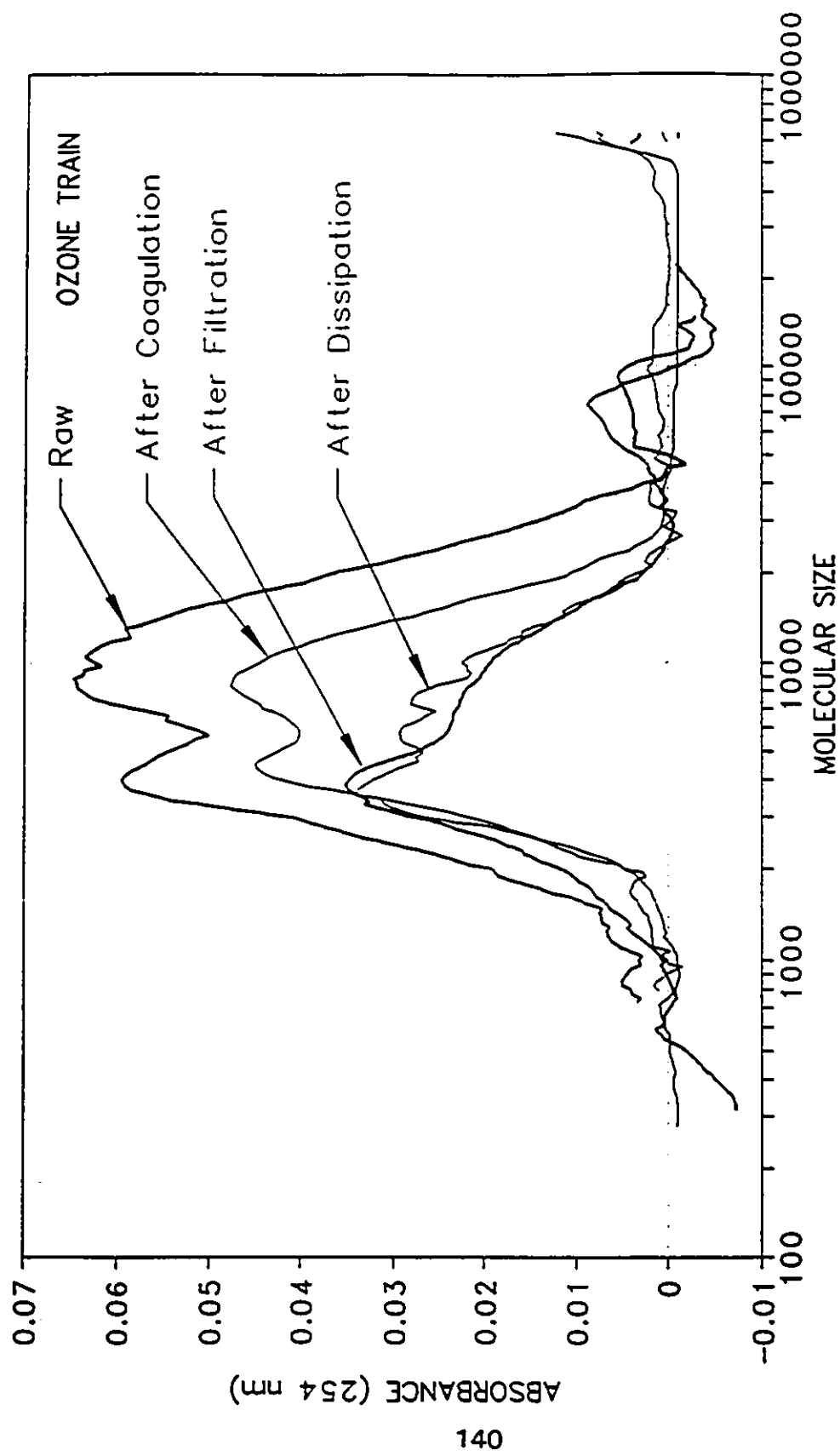


Figure 6.4. GPC-AMSD of humic substances, ozone train.

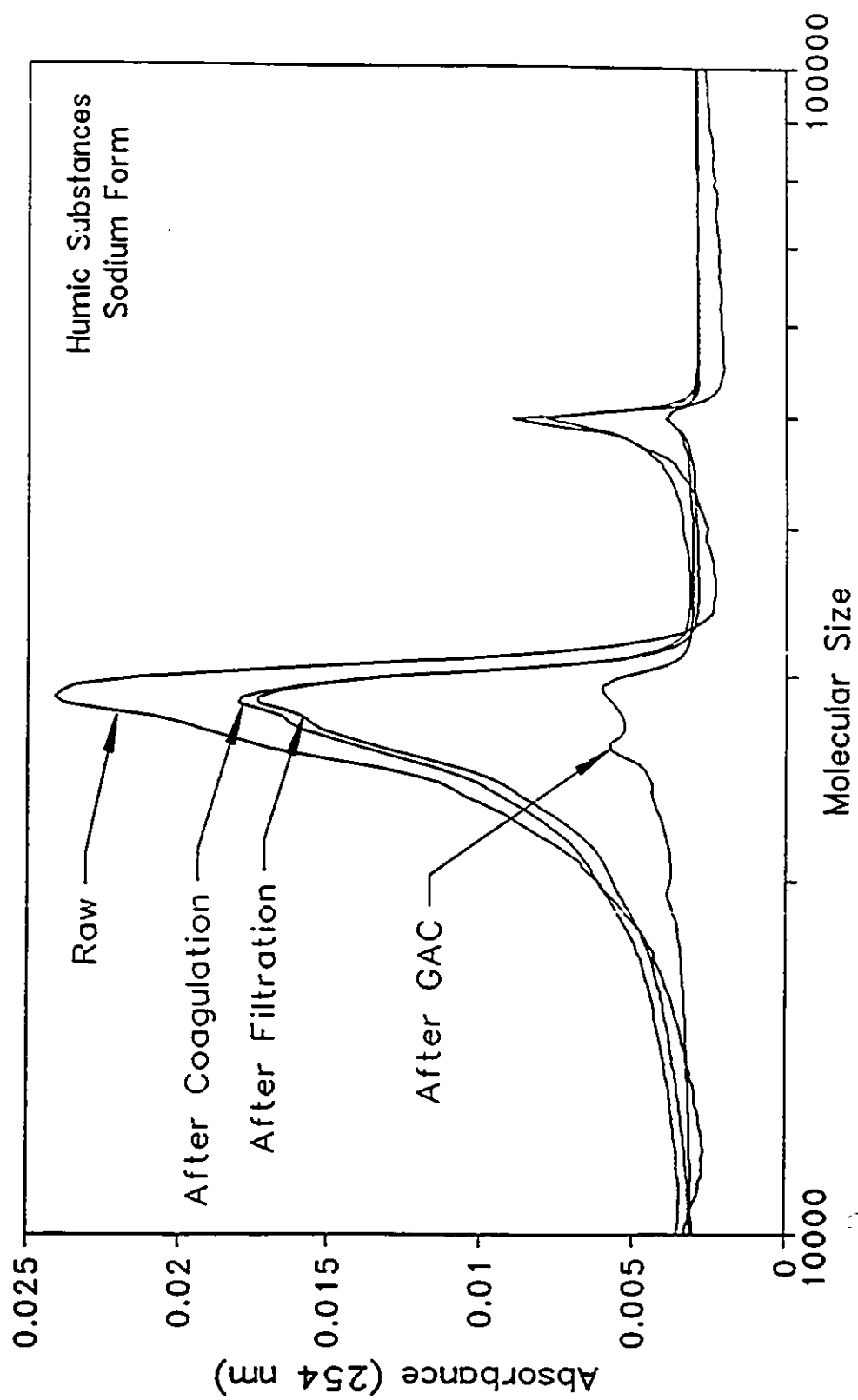


Figure 6.5. HPSEC-AMSD of humic substances, chlorine train (sodium form).

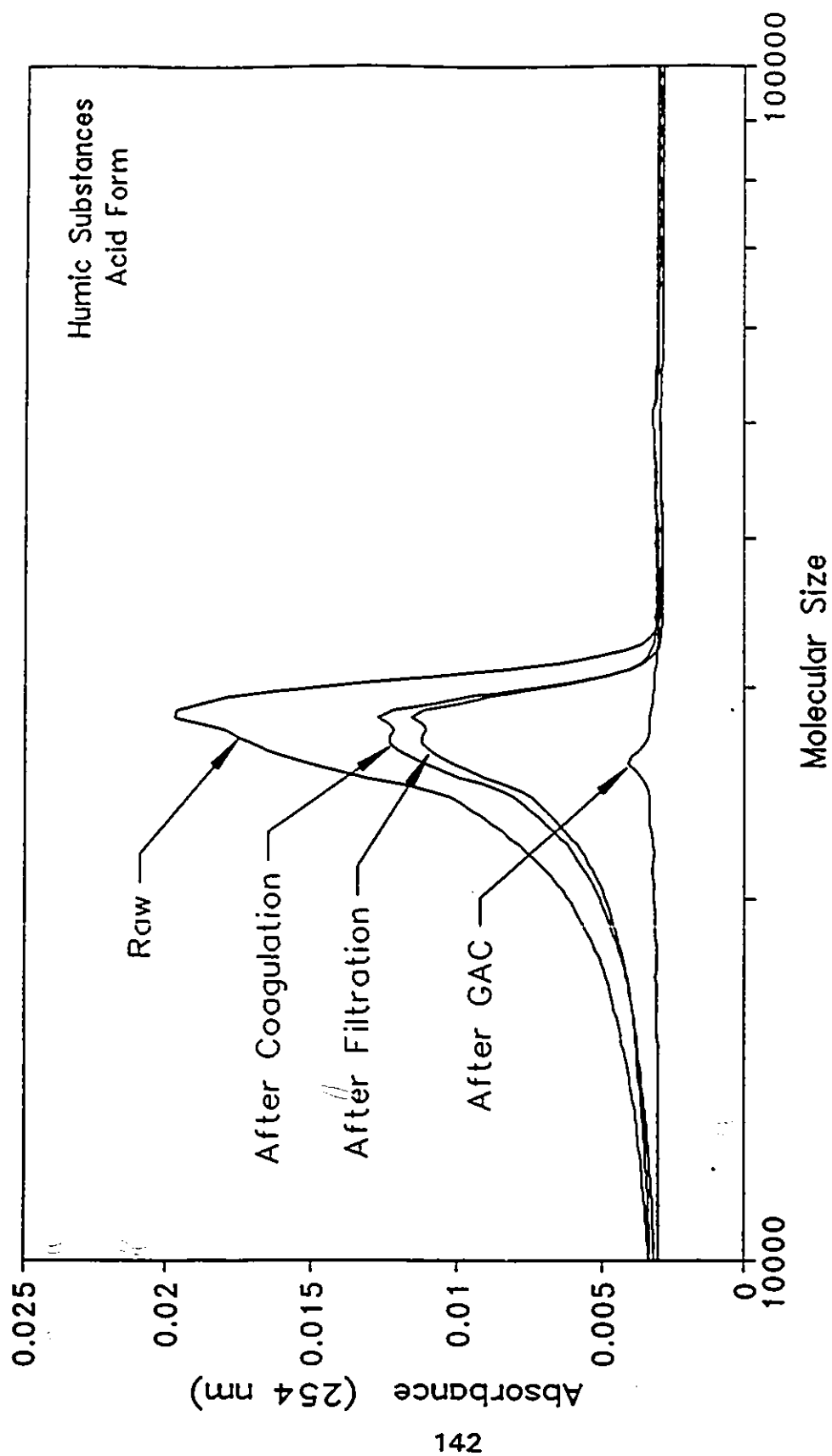


Figure 6.6. HPSEC-AMSD of humic substances, chlorine train (acid form).

was reflected in the AMSD. The filtration process in the chlorination train caused the same effect of reduction without apparent alteration in the distribution. The GAC was observed to be the most effective process in the removal of THM precursors and a change in the distribution of the molecular size was detected in the sodium form. This alteration in the molecular size distribution can be a result of the removal process itself and was reflected by interactions of the column material with the new composition of the humic substances.

In the AMSD chromatograms of the ozone train, after ozonation, a large change in the AMSD was detected. This change was also affected by the composition of the humic substances (acid or base forms). The breakdown into components of different sizes was detected in both the sodium and the acid AMSD chromatograms. In the sodium form, these components appeared to occur in the same quantity, but in the acid form, the smaller size was more prevalent than the larger size (Figures 6.7 and 6.8). After filtration, both chromatograms show that some of the lower molecular size groups were removed. These observations can be associated with the fact that ozone, as a strong oxidant, reacts with the organic matter producing compounds of different chemical composition characterized by a lower molecular size. After the GAC process, the same two groups of compounds appeared in the sodium form but in much smaller quantities.

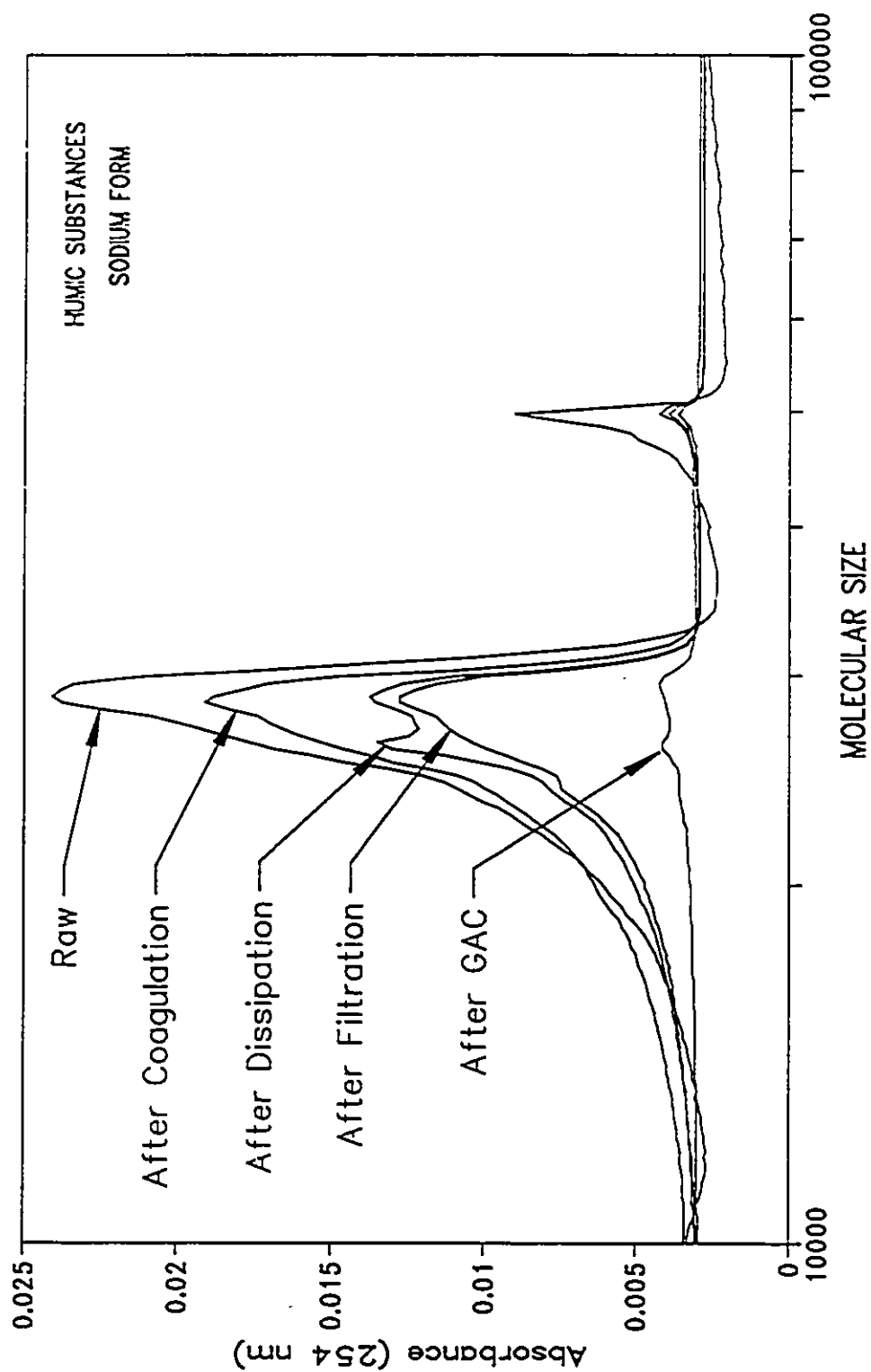


Figure 6.7. HPSEC-AMSD of humic substances, ozone tram (sodium form).

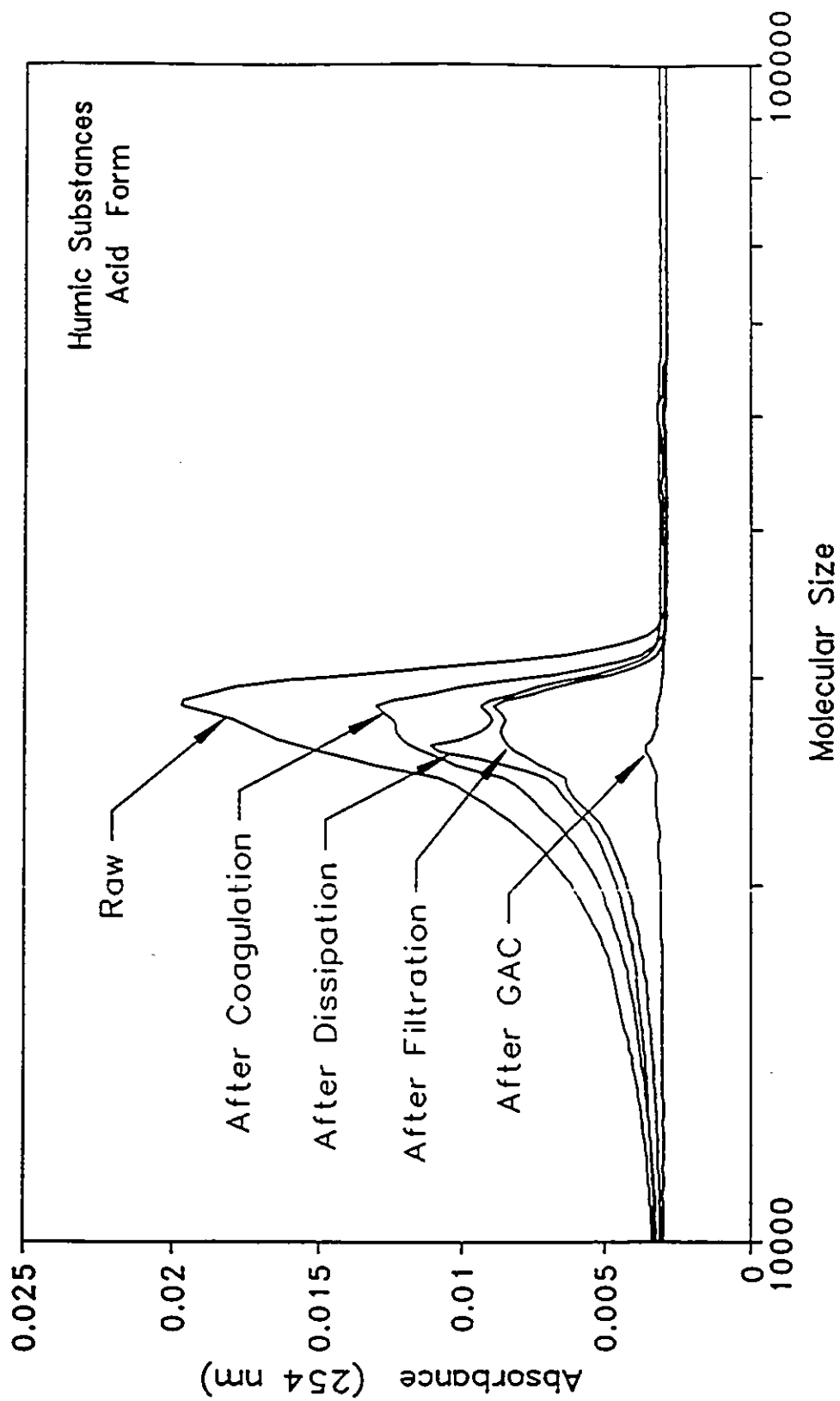


Figure 6.8. HPSEC-AMSD of humic substances, ozone train (acid form).

6.5. Trihalomethane Formation Potential

The THMFP was determined for all the samples and their non-humic fractions along both treatment trains in order to estimate the effect of precursor removal on the THMFP after each process.

6.5.1. Chlorine Consumption

The chlorine consumption of all the samples was determined by chlorinating the samples with a 10 mg/L chlorine dosage and measuring the residual chlorine in the samples after 0.2, 1, 2, 4, and 7 days. Results are shown in Figures 6.9 and 6.10 for both trains. It can be seen that the effect of precursor removal on the chlorine consumption is significant. There is more than a 50 percent reduction in chlorine consumption between the overall sample and the non-humic fraction. A difference in consumption was observed for each of the different processes and the lowest consumption was detected for the non-humic fraction of the GAC sample.

It was observed from the above study that the chlorine dosage of 10 mg/L maintained a positive residual chlorine after a 7 day incubation period in all the samples. Therefore, the same chlorine dosage was used to measure the THMFP under the constant driving force of chlorine and to compare the THMFP in both the non-humic fraction and the overall samples. It is recognized that the non-humic fractions consume less chlorine and that the probable effect of a higher than required chlorine dosage in the non-humic fraction would result in a higher THMFP response.

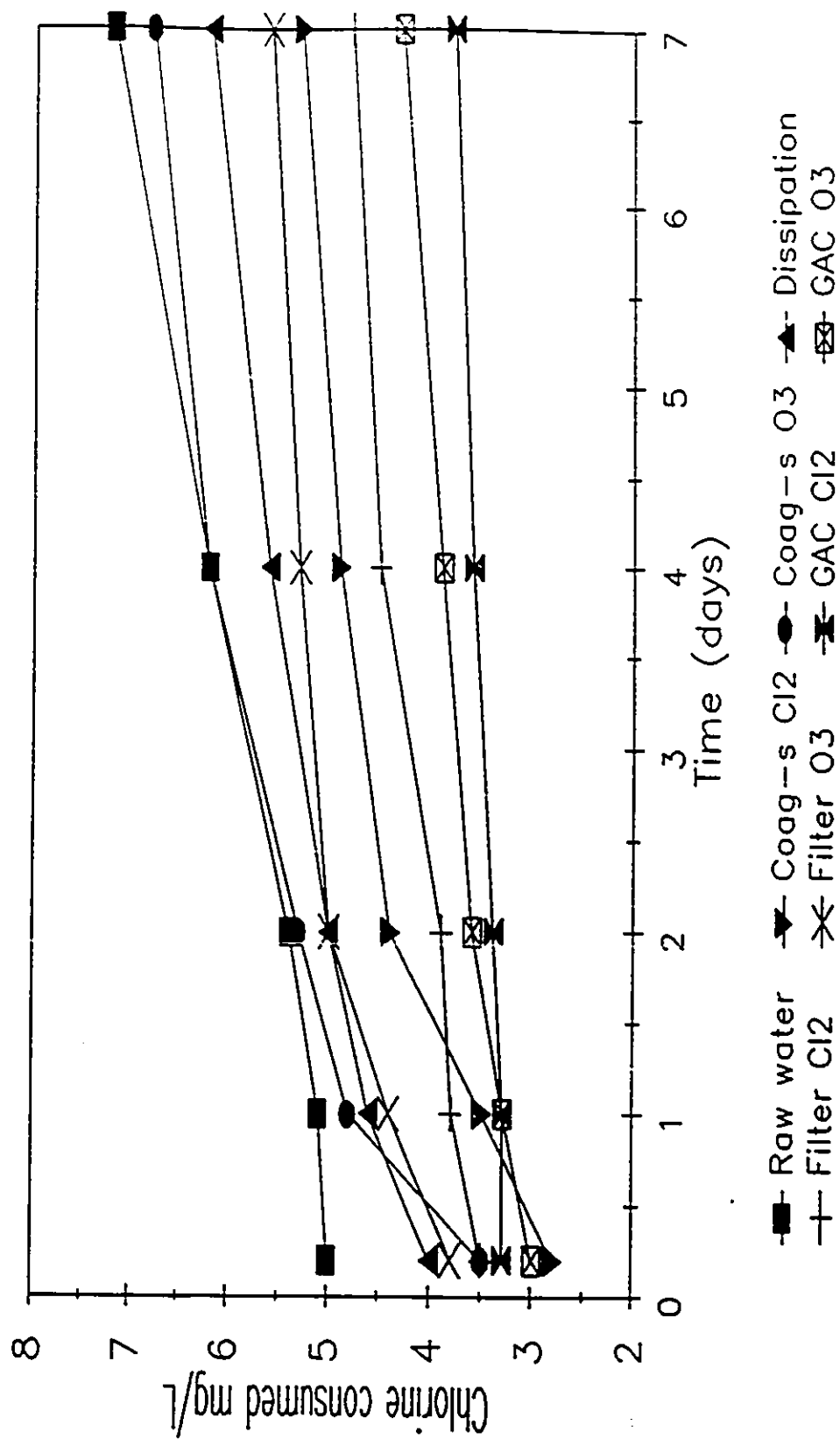


Figure 6.9. Chlorine consumption by untreated and treated samples, chlorine and ozone trains.

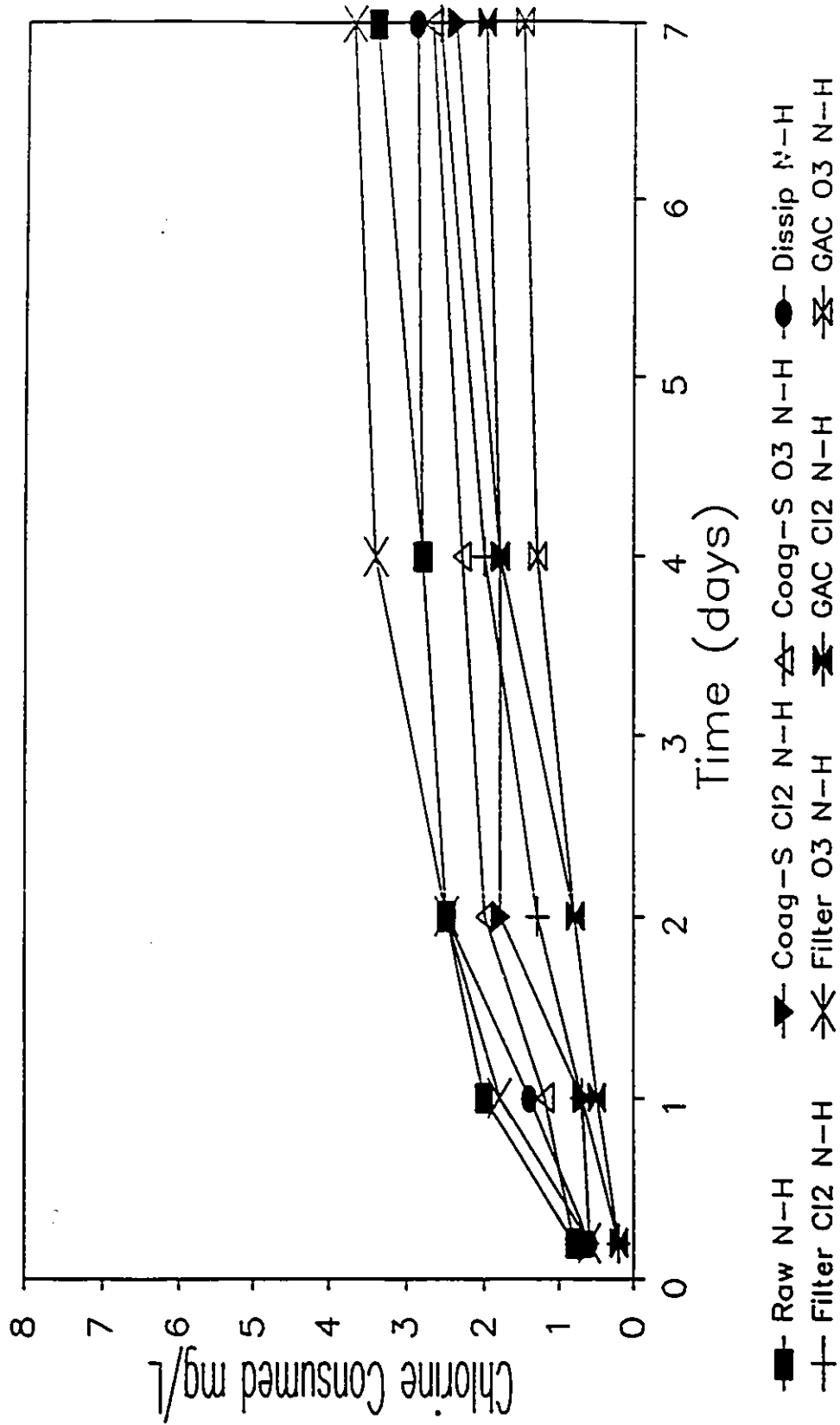


Figure 6.10. Chlorine consumption by the non-humic fraction of untreated and treated samples, chlorine and ozone trains.

The THMFPs of all the samples were determined as a function of time. Representative curves of THMFP versus time for each process are shown in Figures 6.11 and 6.12 for the chlorine and ozone trains, respectively. As expected, the treatments reduced the THMFP of the raw water for all the reaction times. Figures 6.13 and 6.14 show the THM formation rates versus time. These rates were calculated from the changes in THM concentrations in each time interval (Figures 6.11 and 6.12). There are three zones clearly defined. The highest zone corresponds to the conventional treatment in both chlorine and ozone trains. The medium zone corresponds to the non-humic fractions from the conventional processes and the lowest zone corresponds to the GAC sample and its non-humic fraction.

The chlorine consumption and THM formed after 7 days together with corresponding DOC concentrations are presented in Figure 6.15. The ratios of the THMFP of treated water to the THMFP of the raw water over the various reaction times were calculated to determine if the THM formation was affected by the different processes. Results are plotted in Figure 6.16 and 6.17. The THMFP after coagulation-sedimentation and filtration processes in the chlorine train appears to be higher than the corresponding raw water in the first four hours. However, it decreases rapidly with time. The THMFP after the GAC treatment both for the sample and the non-humic fractions are markedly low and constant with time.

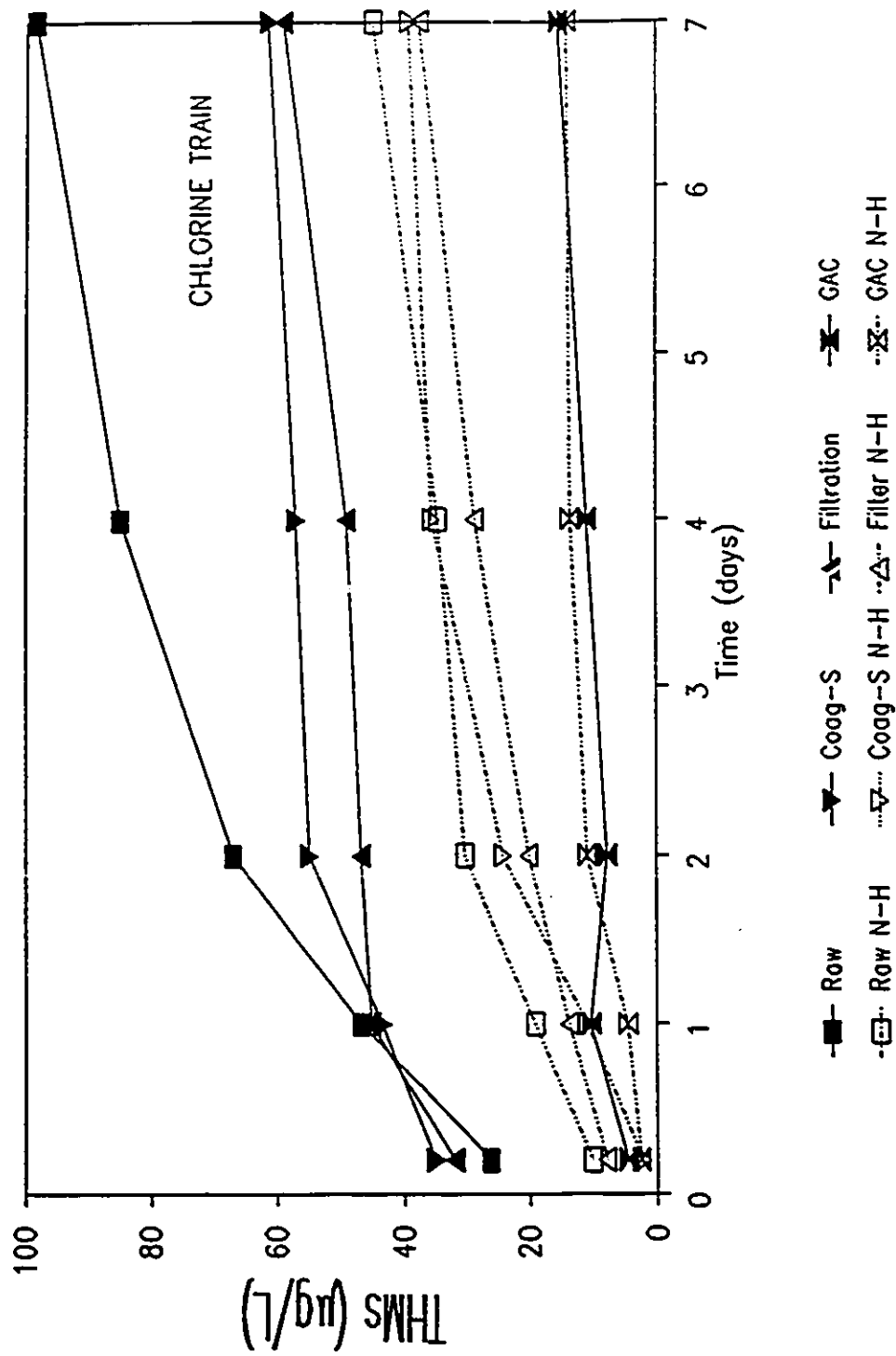


Figure 6.11. THMFP of untreated and treated samples and their corresponding non-humic fractions, chlorine train

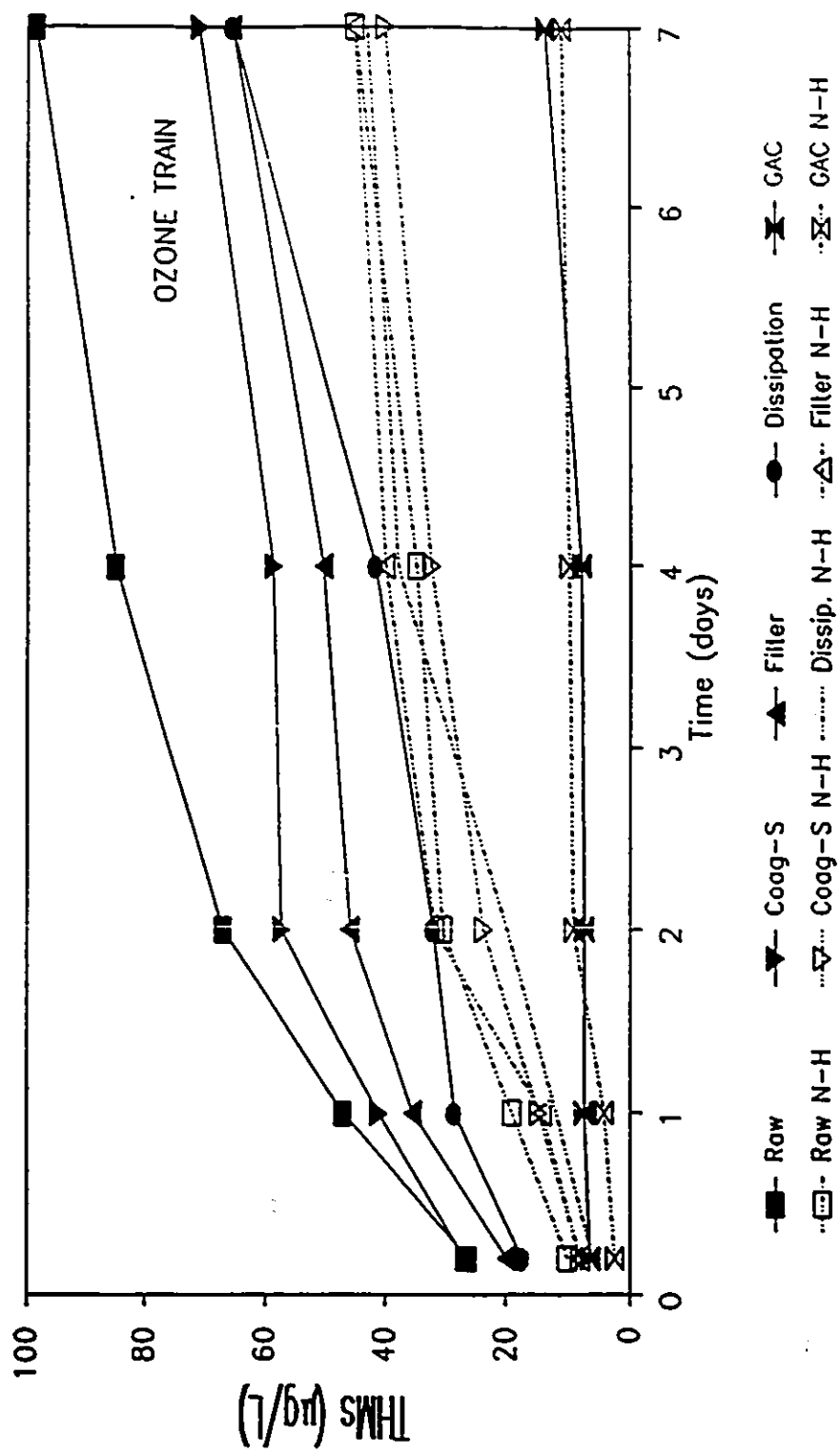


Figure 6.12. THMFP of untreated and treated samples and their corresponding non-humic fraction, ozone train.

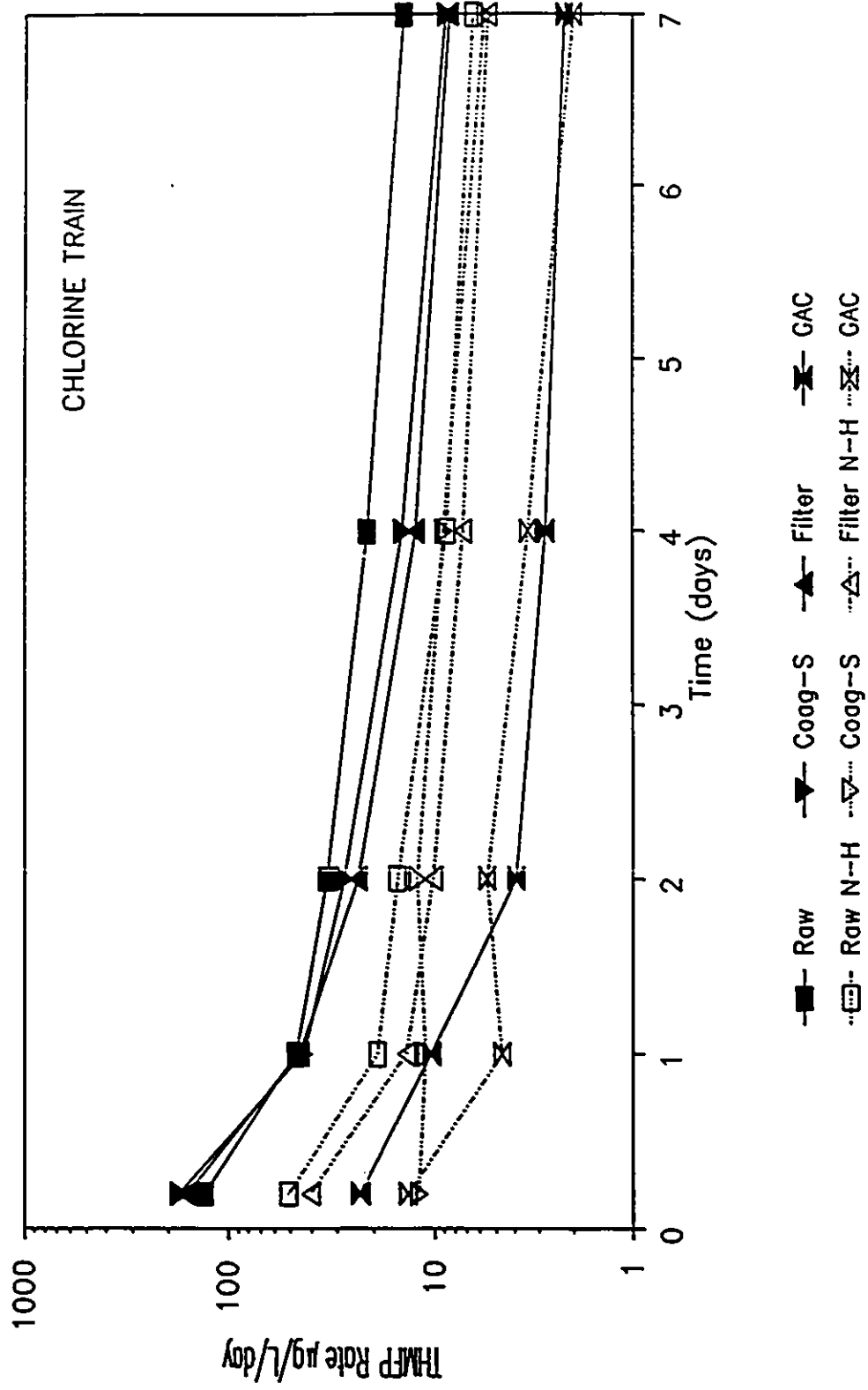


Figure 6.13. THMFP rate of samples and their non-humic fraction, chlorine train.

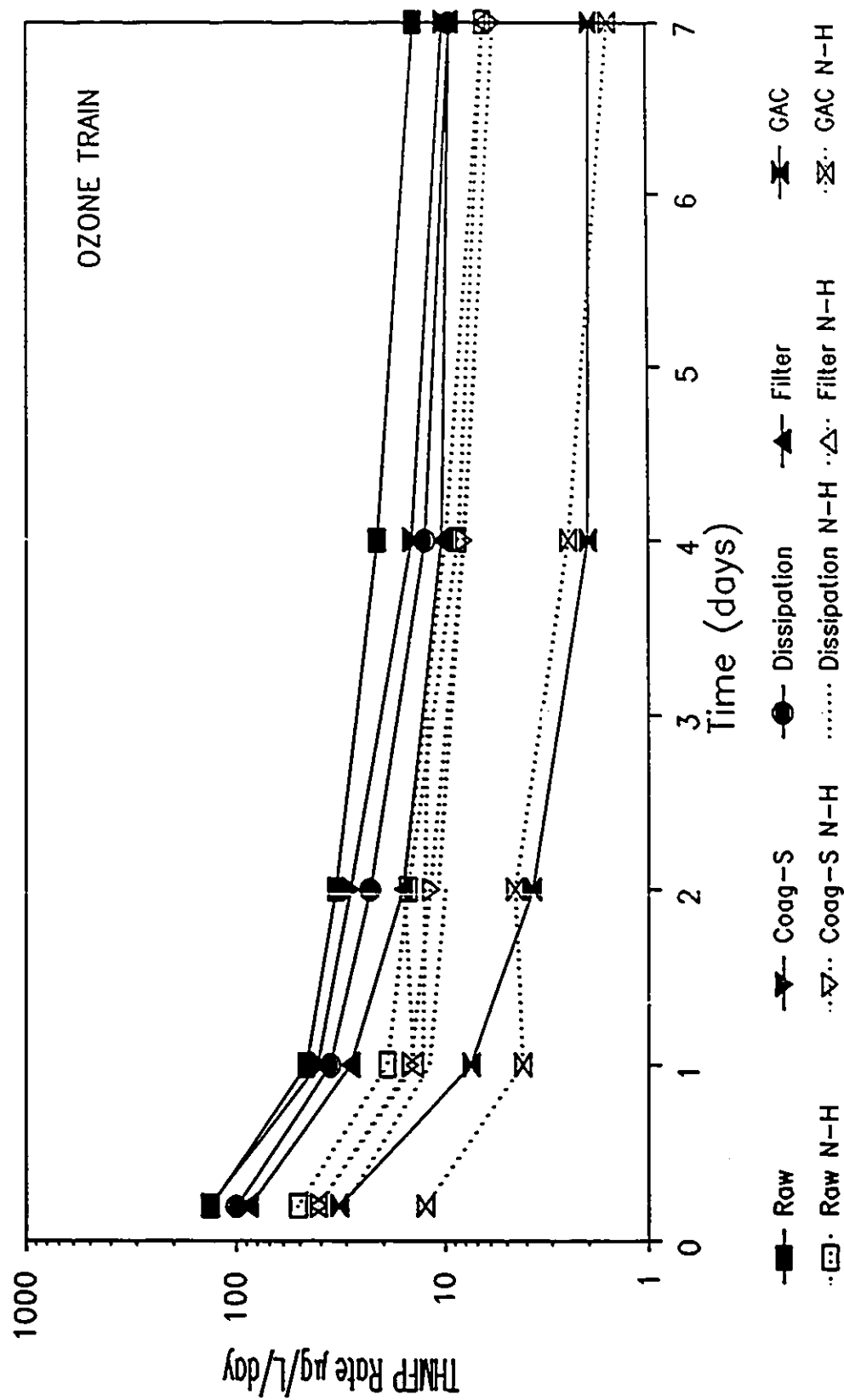


Figure 6.14. THMFP rate of samples and non-humic fraction, ozone train.

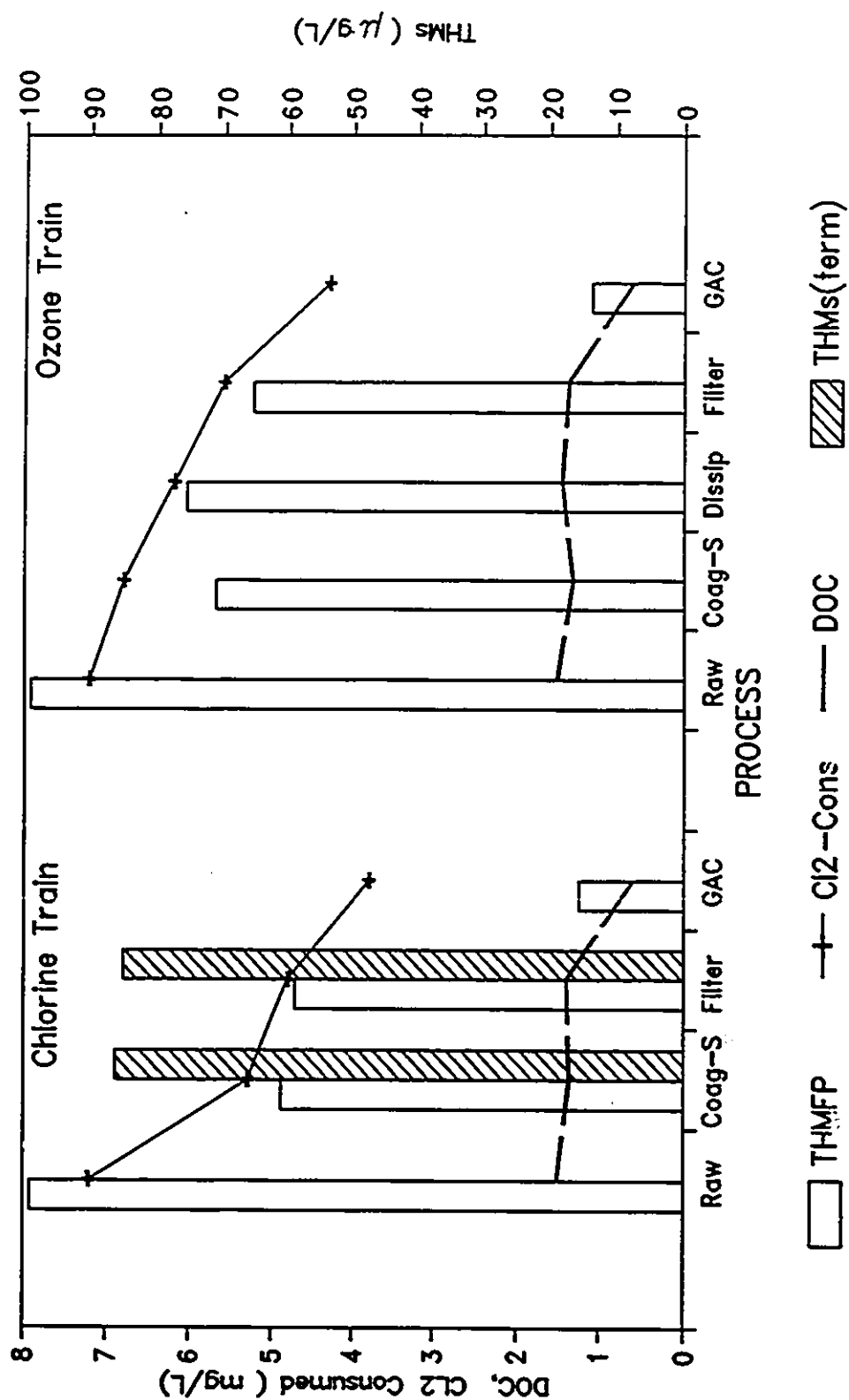


Figure 6.15. THMFP, DOC and chlorine consumption for different processes along the pilot plant.

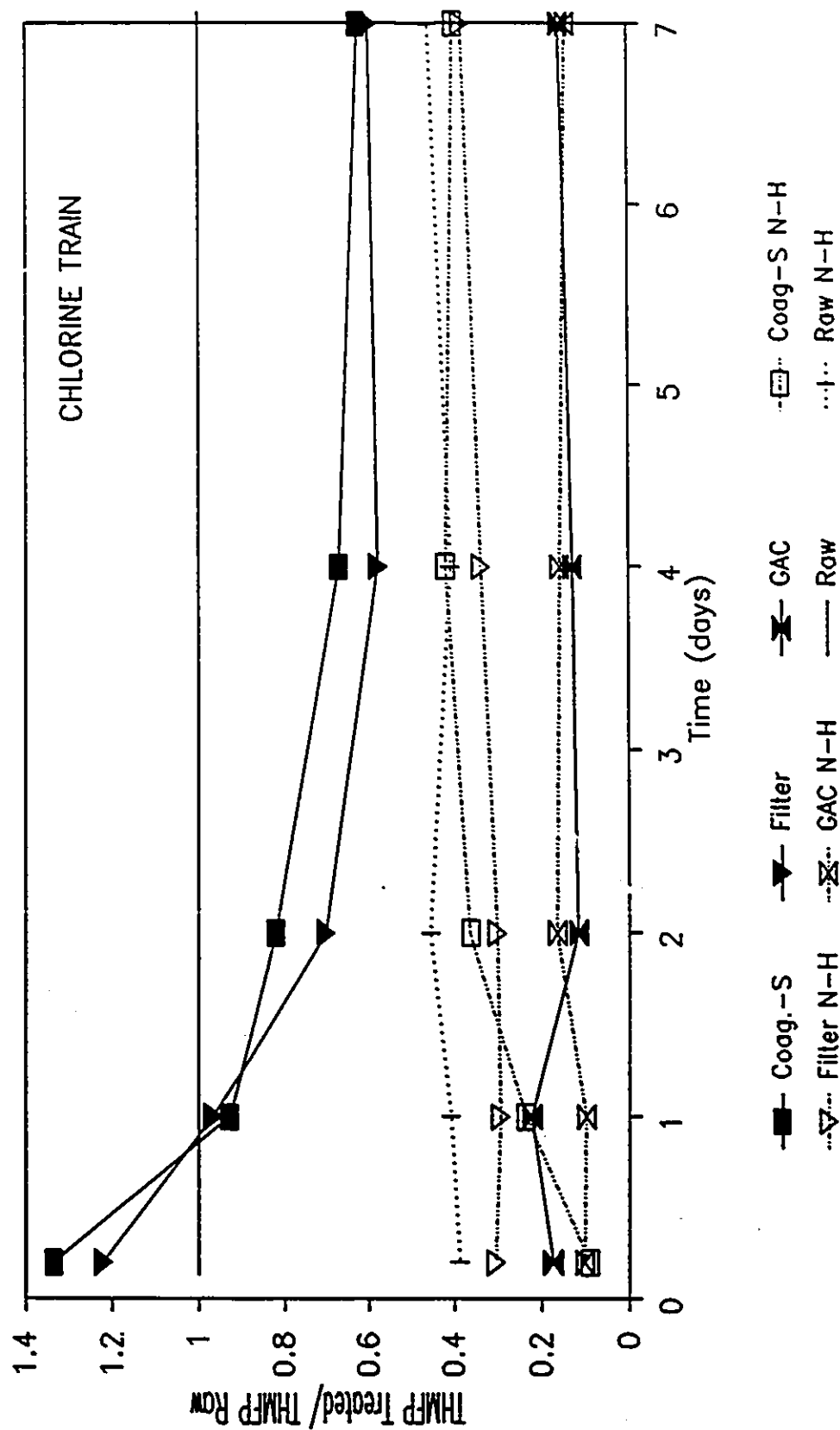


Figure 6.16. Effect of different treatment processes on kinetics of THM formation, chlorine train.

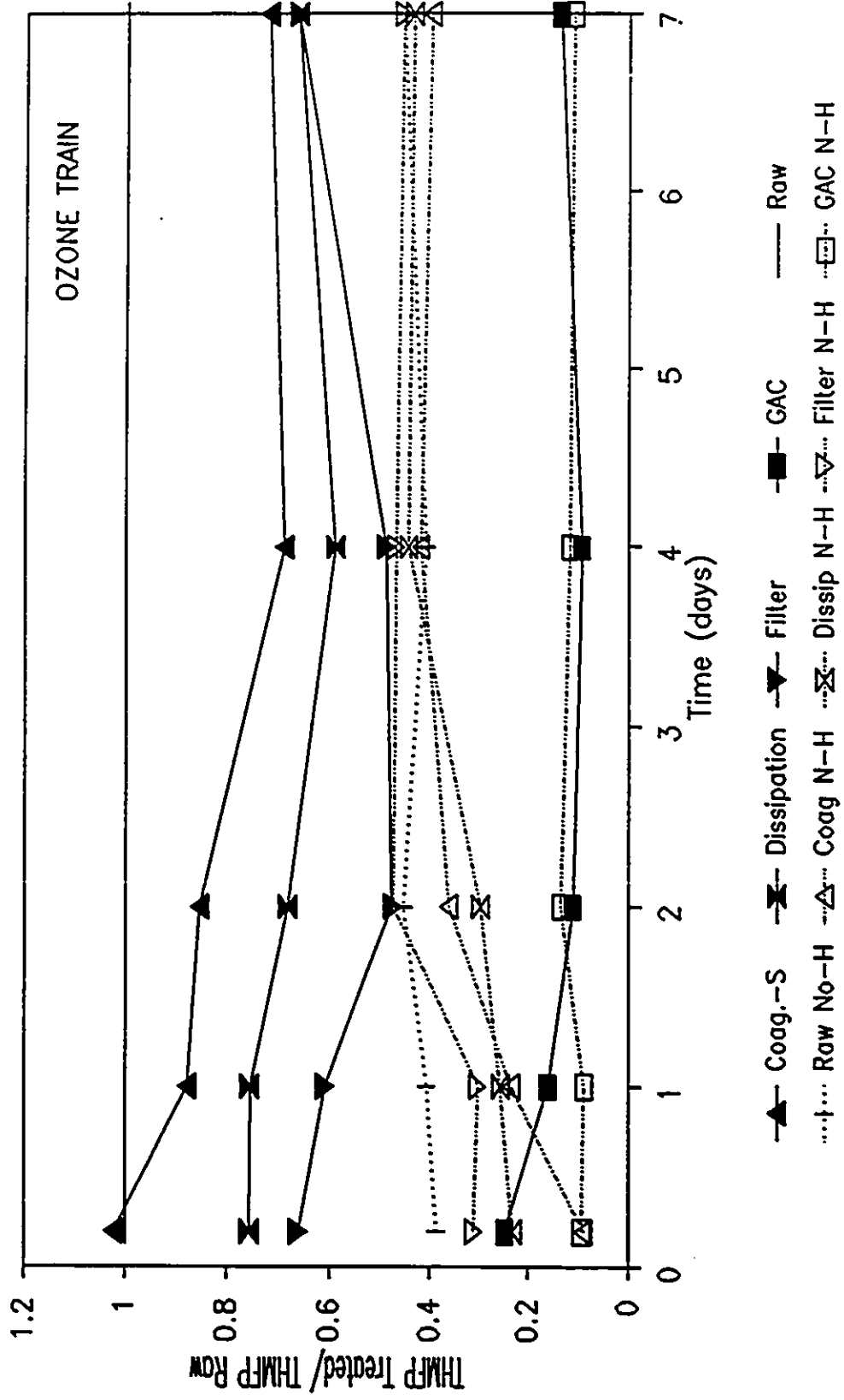


Figure 6.17. Effect of different treatment processes on kinetics of THM formation, ozone train.

6.5.2. THM Reactivities

The THM reactivities or yields, expressed in terms of $\mu\text{g THM/mg C}$, of the untreated and treated waters are summarized in Table 6.3. It can be seen that the untreated water has the higher reactivity. After coagulation-sedimentation, there was a decrease in reactivity in both trains but the yield was lower in the chlorine train and was probably caused by the action of the chlorine as an oxidant at the prechlorination stage. At this point, no oxidant was added to the water in the ozone train. After ozonation, at the dissipation stage, the THM yield decreased, probably due to the oxidation action of ozone. After filtration, both trains showed a slight increase in reactivity. However, since the decrease in reactivity due to coagulation-sedimentation was very low, it is assumed that no change in reactivity took place although the oxidation action of both ozone and chlorine were significant. The GAC reduced the THM reactivity 50 percent when compared to the raw water.

Concentrated humic substances from the untreated samples and the samples from the coagulation-sedimentation process were diluted to a DOC concentration of 2 mg/L. They were then chlorinated and analyzed for THMFP. Results indicated that the THM yield was practically the same as that of the overall sample, but was higher than that of the non-humic fractions. This confirms the importance of humic substances as primary contributors of THM precursors in natural waters, as reported in the literature (Edzwald, 1987; Amy *et al.*, 1992).

The THM yield of the non-humic fraction shows that, as anticipated, this was lower than that of the overall sample, but was not negligible. Even a direct comparison

Table 6.3. Trihalomethane reactivities/yields of untreated and treated water samples (October 1993).

Sample	Original Water				Humic Fraction				Non-Humic		
	DOC mg/L	THMFP µg/L	THM/DOC µg/mg	DOC mg/L	THMFP µg/L	THM/DOC µg/mg	DOC mg/L	THMFP µg/L	THM/DOC µg/mg	THMFP µg/L	THM/DOC µg/mg
Chlorination	Raw	2	98.5	49	2	96	48	1.5	45	30	
	Coag Sedim	1.75	61.5	35	2	90	45	1.35	40	30	
	Filter	1.58	59	37				1.39	38	27	
	GAC	0.63	15.5	25				0.61	14	23	
Ozonation	Raw	2	98.5	49	2	96	48	1.5	45	30	
	Coag Sedim	1.71	71	42	2	100	50	1.32	40	30	
	Disinip O ₃	1.65	65	39				1.46	43	29	
	Filter	1.6	65	41				1.38	45	33	
	GAC	0.62	13.6	22				0.61	11	18	

with the overall sample reactivity provides no conclusive answer. The results show again that there was a significant contribution of the non-humic fraction to both the THMFP and the DOC. Lower THM reactivities than those observed for the other non-humic fraction samples were detected for the GAC sample. These results confirm the high efficiency of GAC in the removal of both humic and non-humic THM precursors.

Chapter VII

CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions

The following conclusions may be drawn from this study:

- ▶ A group of compounds with three distinct apparent molecular size distributions (AMSD) was identified by GPC in the raw water;
- ▶ The results show significant seasonal variations in humic substances concentrations and these variations are probably influenced by the turn-over in water bodies, especially in the spring;
- ▶ On average, humic substances accounted for 30 percent of the total DOC in the raw water. The fulvic acid comprised 96 percent of the humic substances, and the remaining 4 percent corresponded to the humic acid;
- ▶ The coagulation-sedimentation process in the conventional treatment was the most efficient treatment process in the reduction of the humic substances. This reduction was achieved primarily through the removal of the medium and low molecular size compounds. However, in terms of efficiency the highest reduction was observed in the high molecular size compounds;
- ▶ No correlation was obtained between the THMFP and the following parameters: DOC, UVA and AMSD.
- ▶ Samples after ozonation showed a shift in molecular size, where a decrease in apparent higher sizes was accompanied by an increase in the lower

apparent molecular size compounds. However, the total reduction of humic substances was similar to that obtained by conventional treatment using chlorine before the coagulation-sedimentation process;

- ▶ The adsorption by GAC was observed to be a very effective process in the reduction of humic substances, DOC, and THMFP;
- ▶ As expected, the reduction in humic substances resulted in lower THMFP levels in the treated water;
- ▶ The HPSEC and the GPC methods can be effectively employed to determine the apparent molecular size fractions of humic materials transformed in a water treatment process.

7.2. Recommendations

Long term monitoring programs are necessary to properly evaluate fluctuations in organic levels in raw water. Further research involving elemental analysis, and determination of the TOX and acidic functional groups are needed to further characterize the humic substances in the water.

Since the GAC process can greatly improve the quality of the treated water, determination of the breakthrough curves for parameters such as THMFP and TOX will provide information that will contribute to determining the viability of this process.

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Appendix A

GPC-AMSD Chromatograms

Figure A.1. GPC-AMSD of humic substances, July 1991.

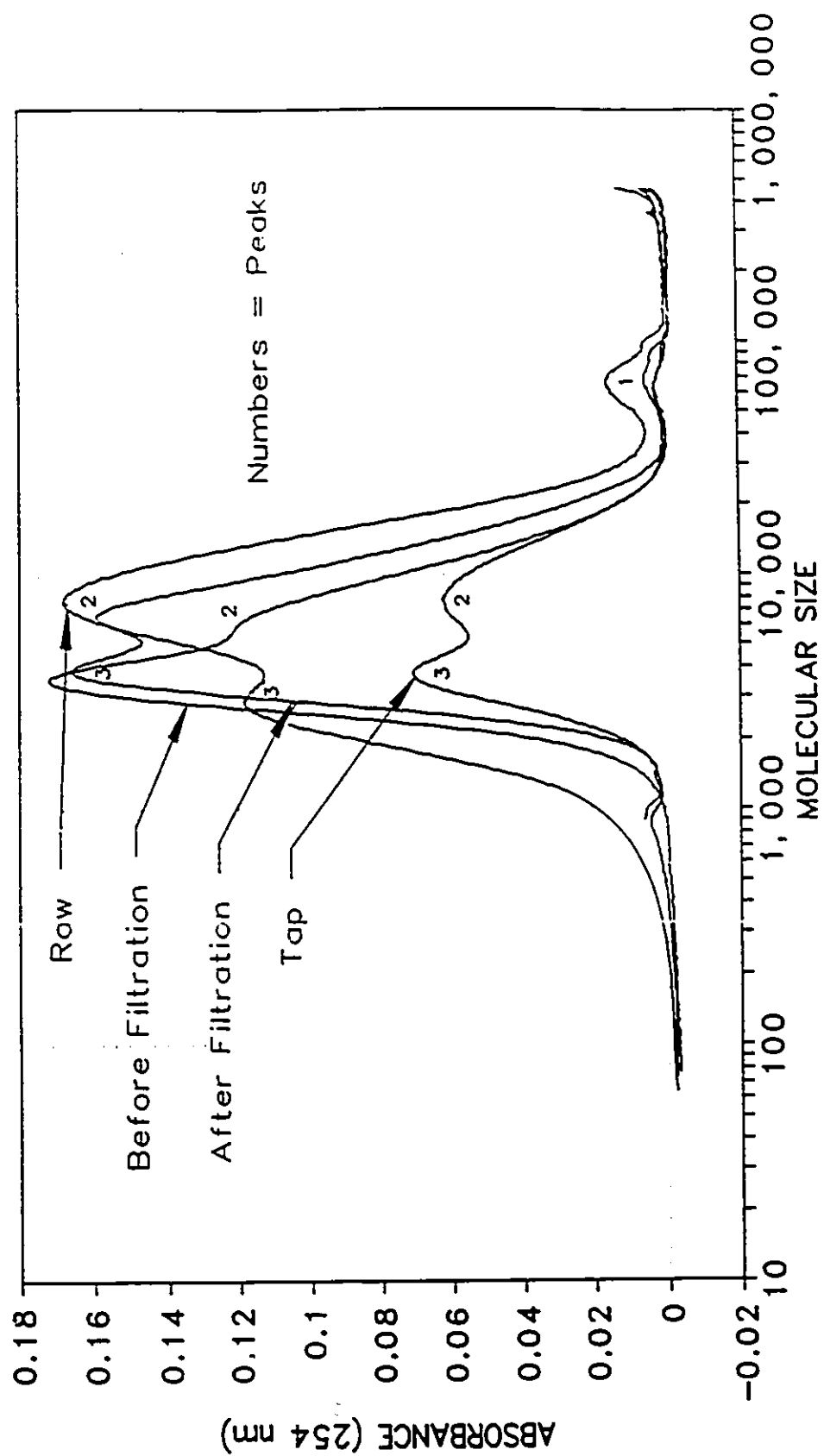


Figure A.2. GPC-AMSD of humic substances, August 1991.

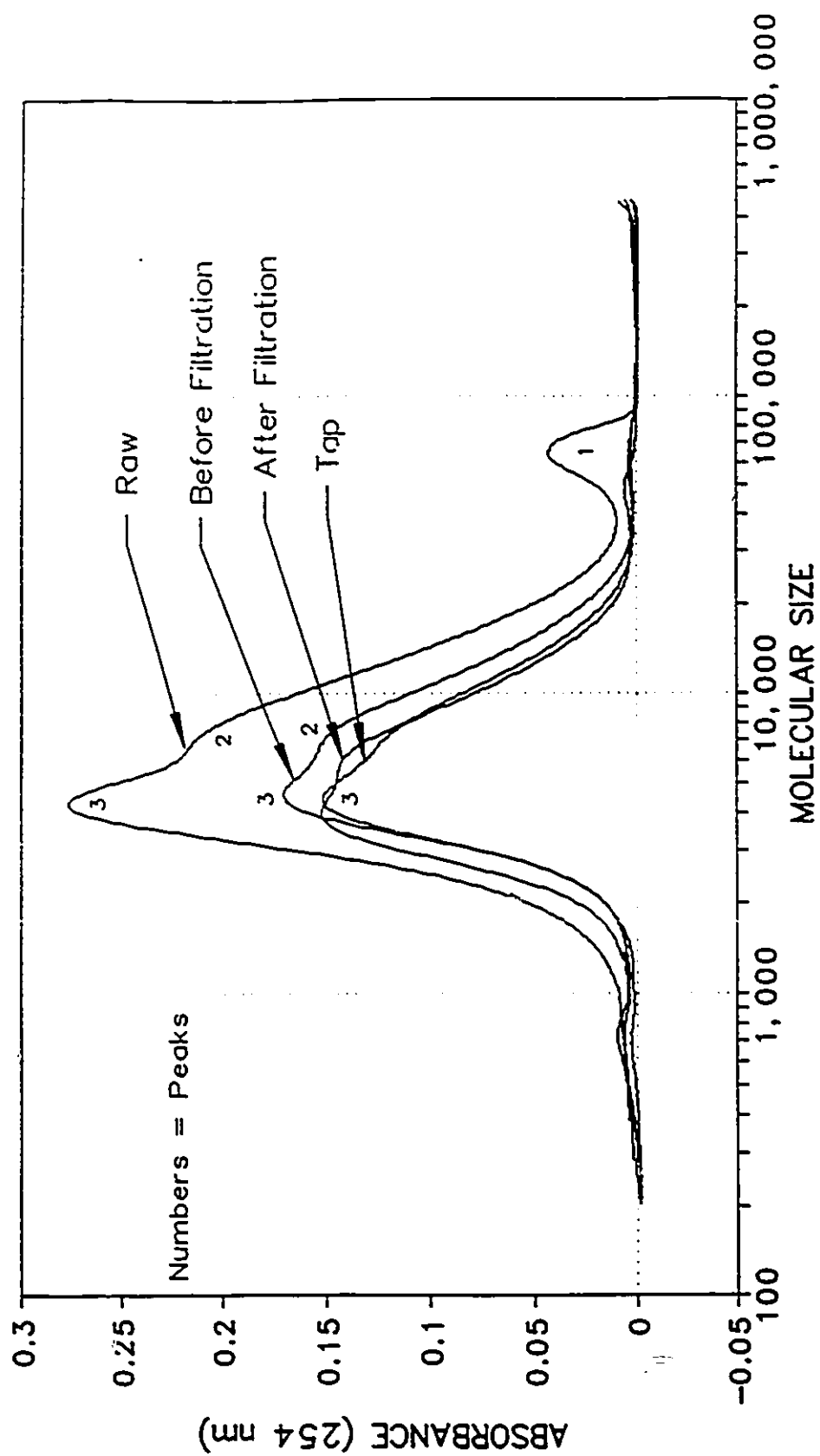


Figure A.3. GPC-AMSD of humic substances, September 1991.

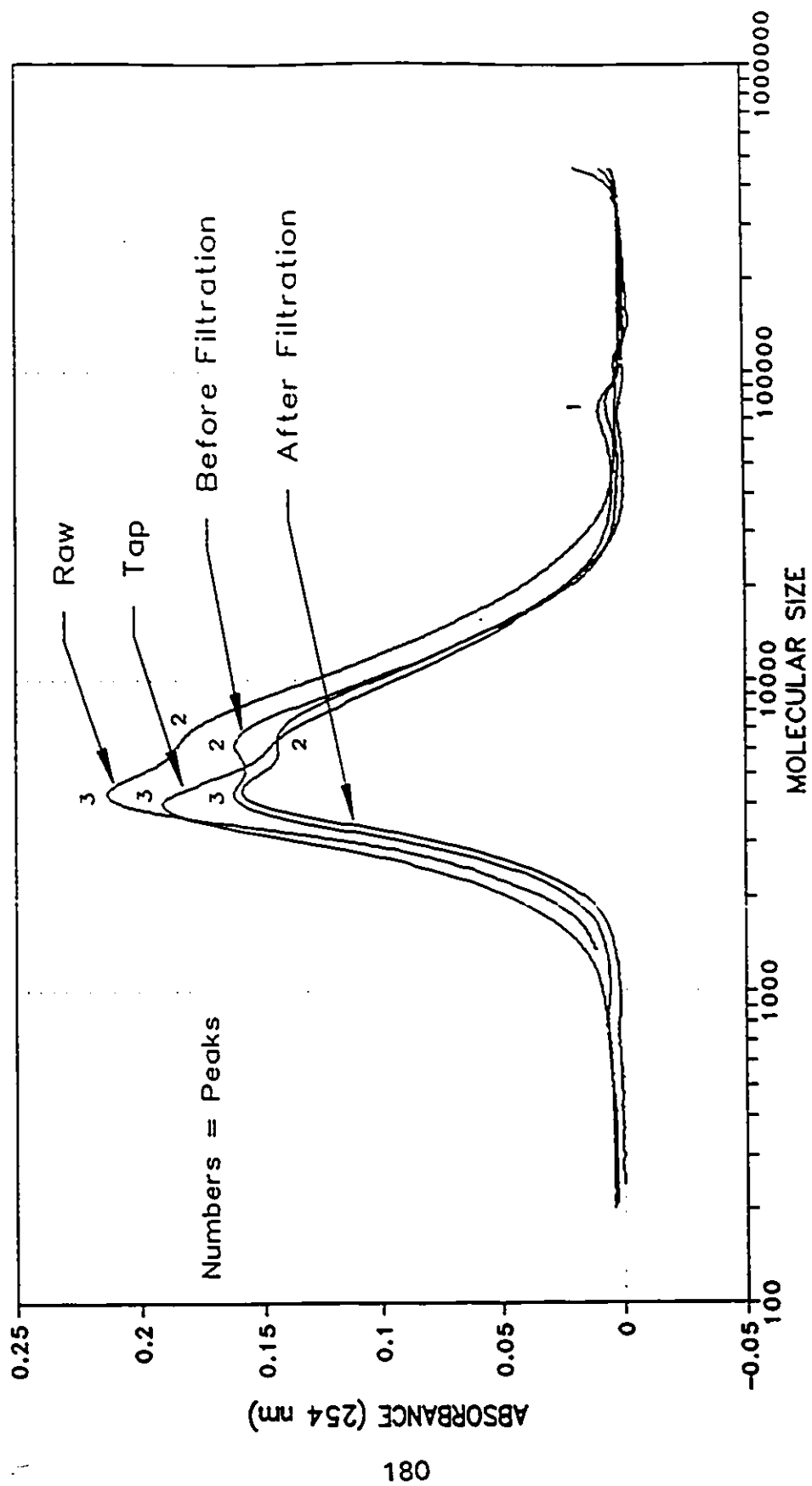


Figure A.4. GPC-AMSD of humic substances, October 1991.

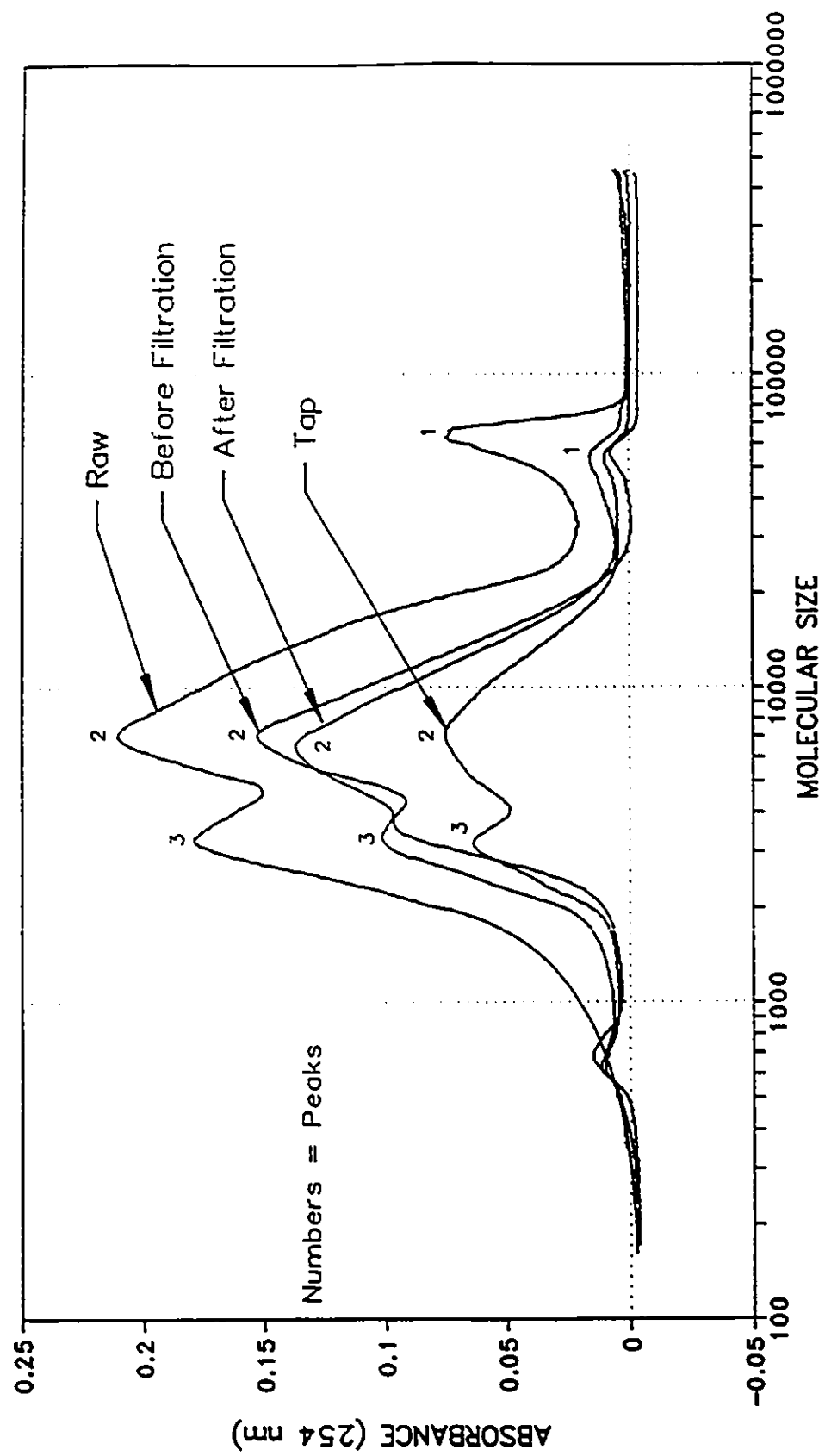


Figure A.5. GPC-AMSD of humic substances, January 1992.

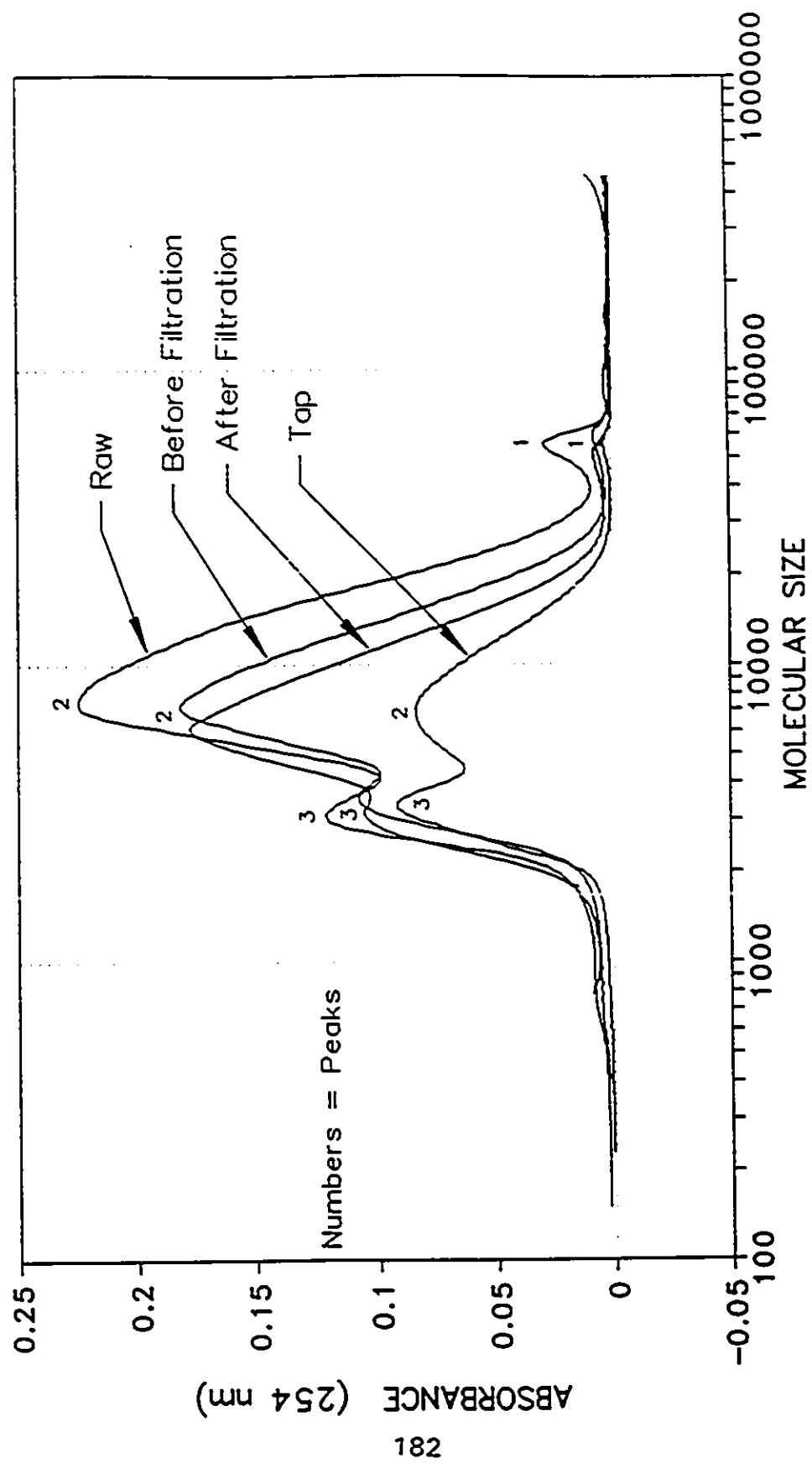


Figure A.6. GPC-AMSD of humic substances, February 1992.

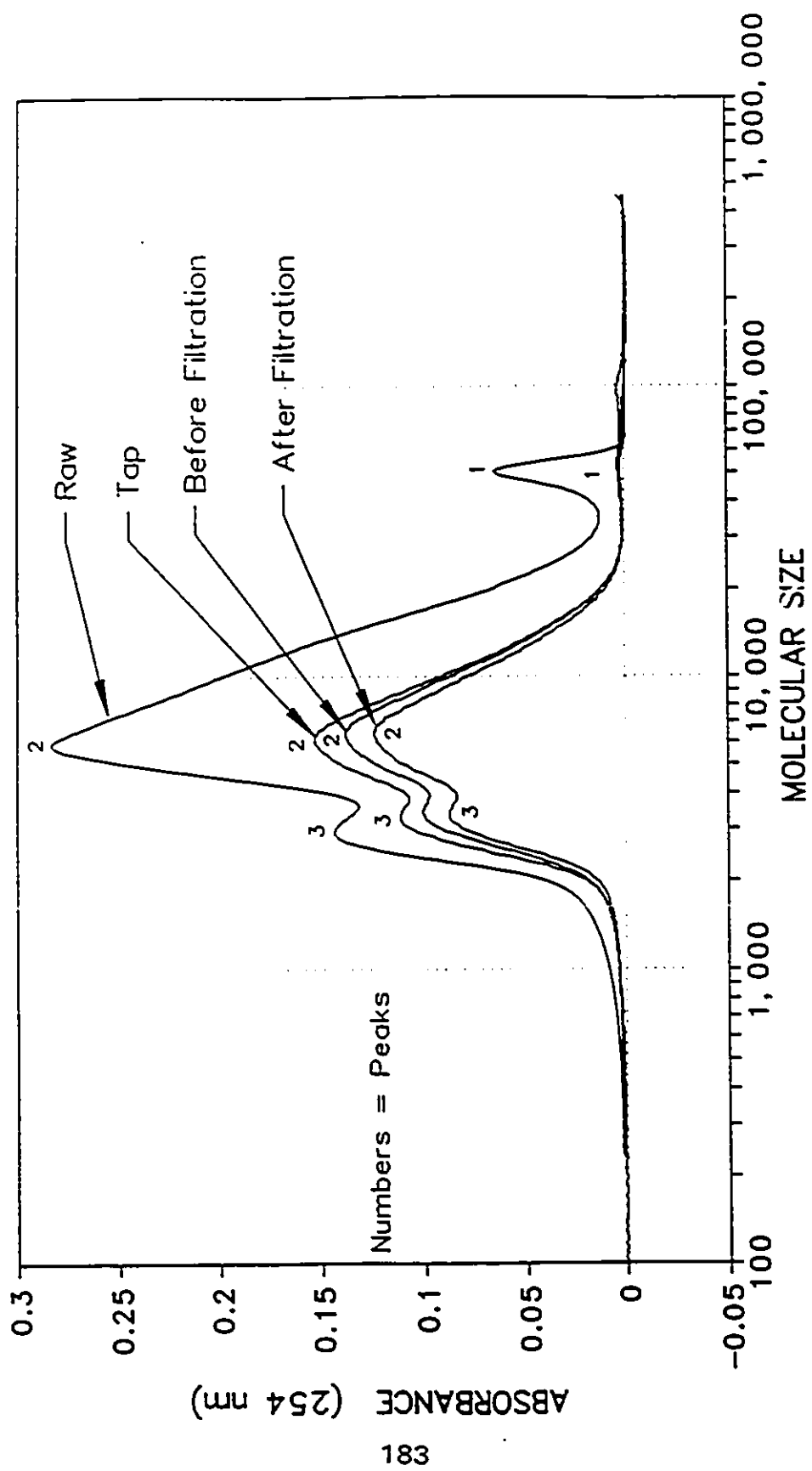


Figure A.7. GPC-AMSD of humic substances, March 1992.

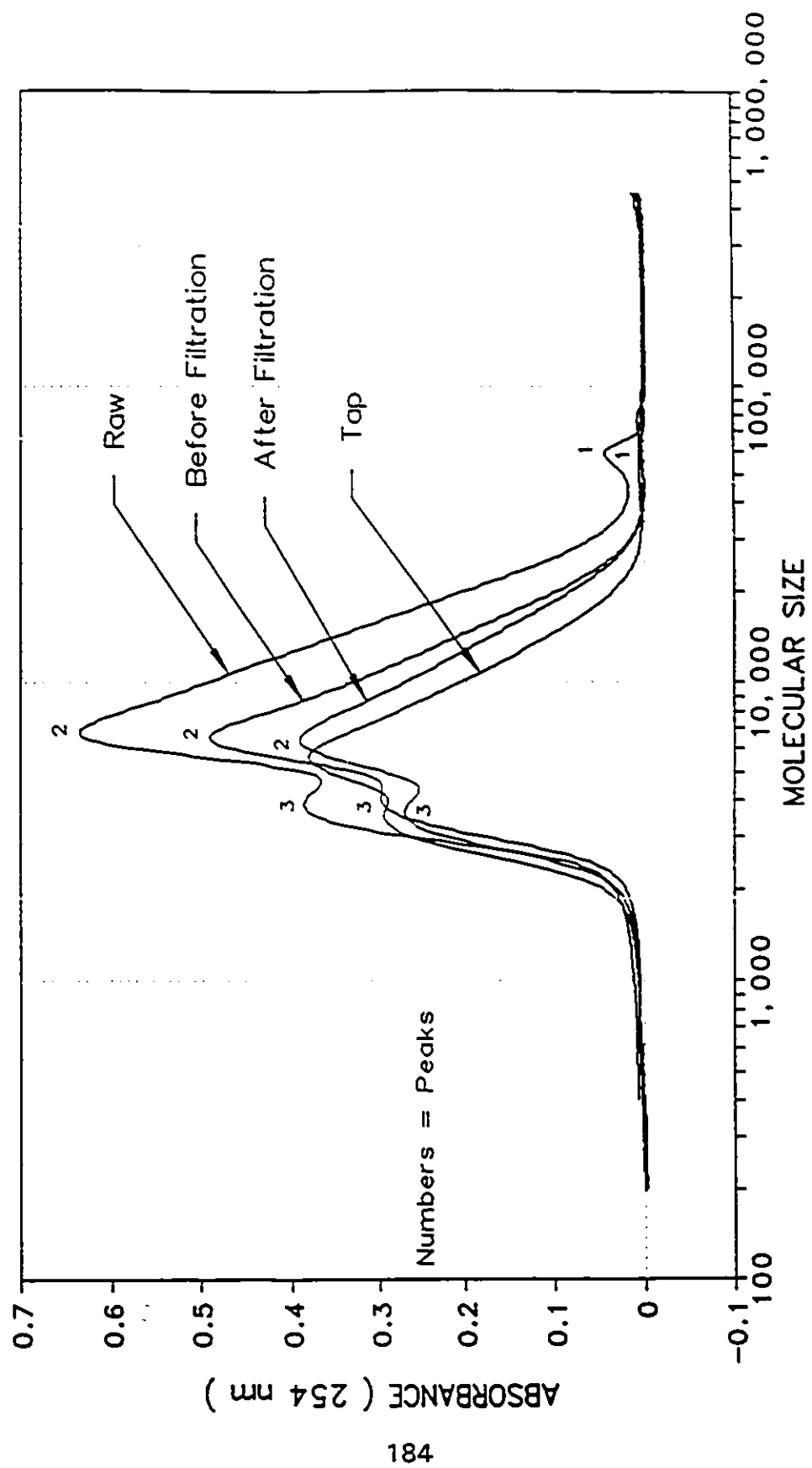


Figure A.8. GPC-AMSD of humic substances, April 1992.

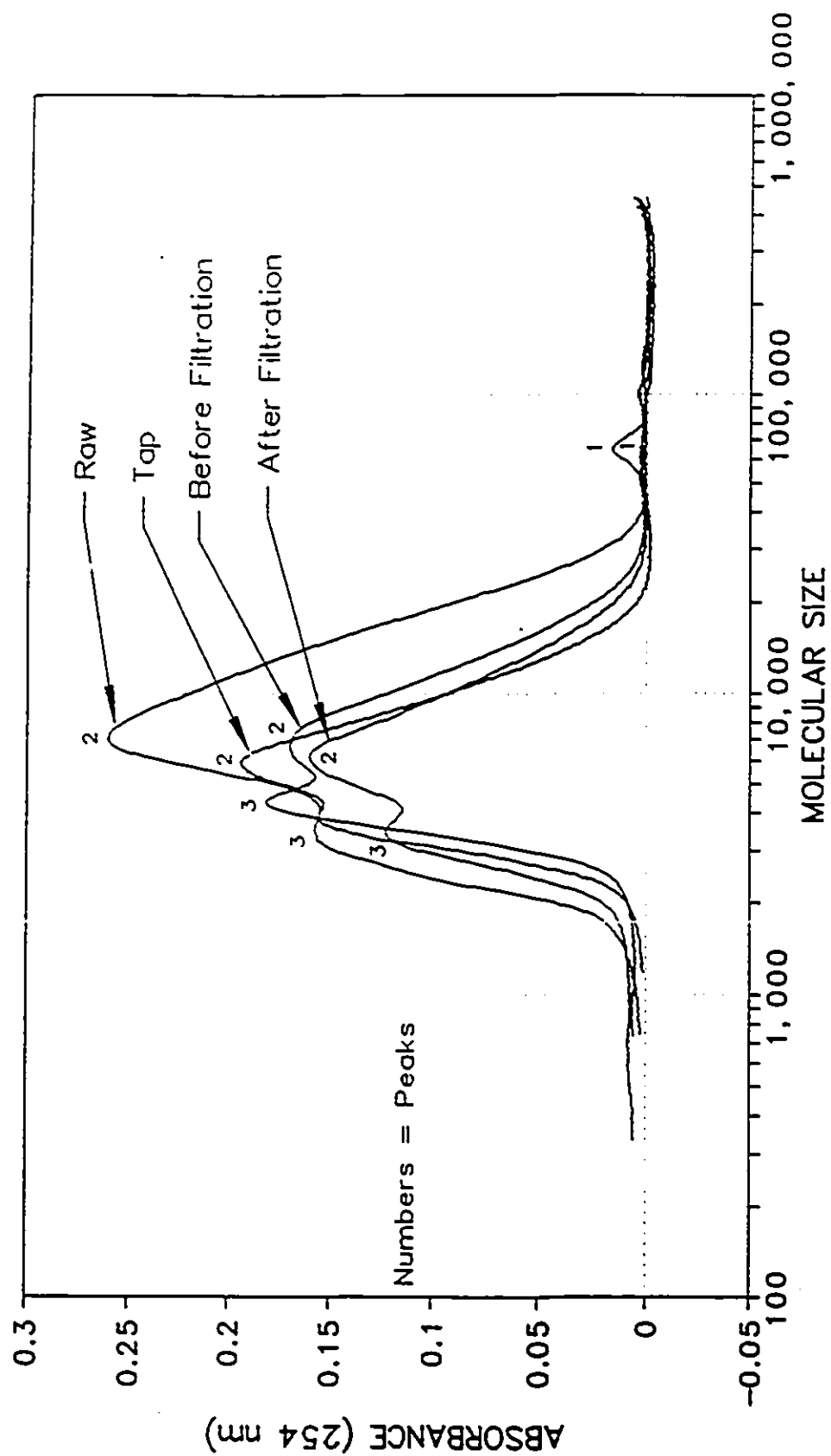


Figure A.9. GPC-AMSD of humic substances, May 1992.

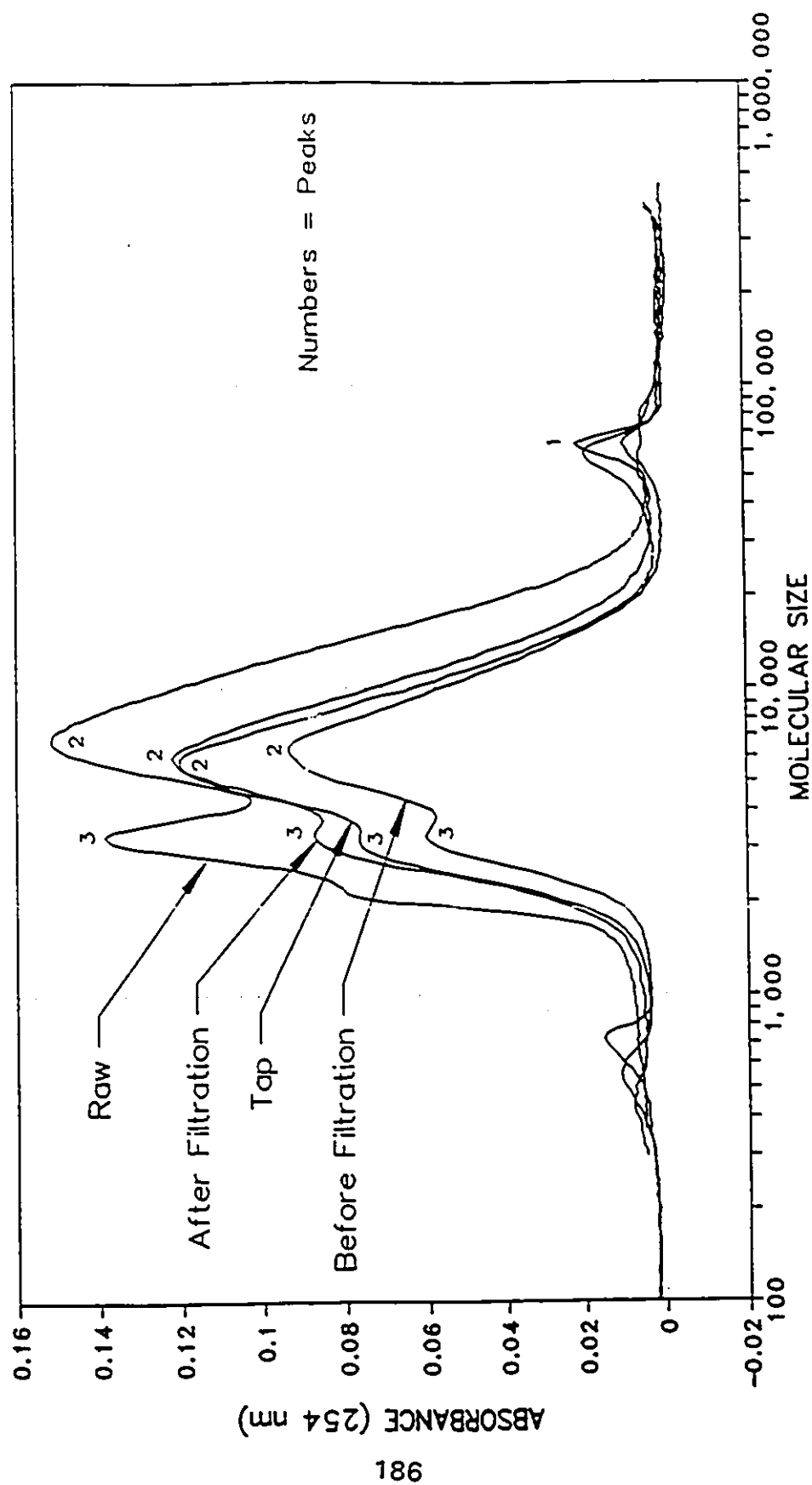


Figure A.10. GPC-AMSD of humic substances, June 1992.

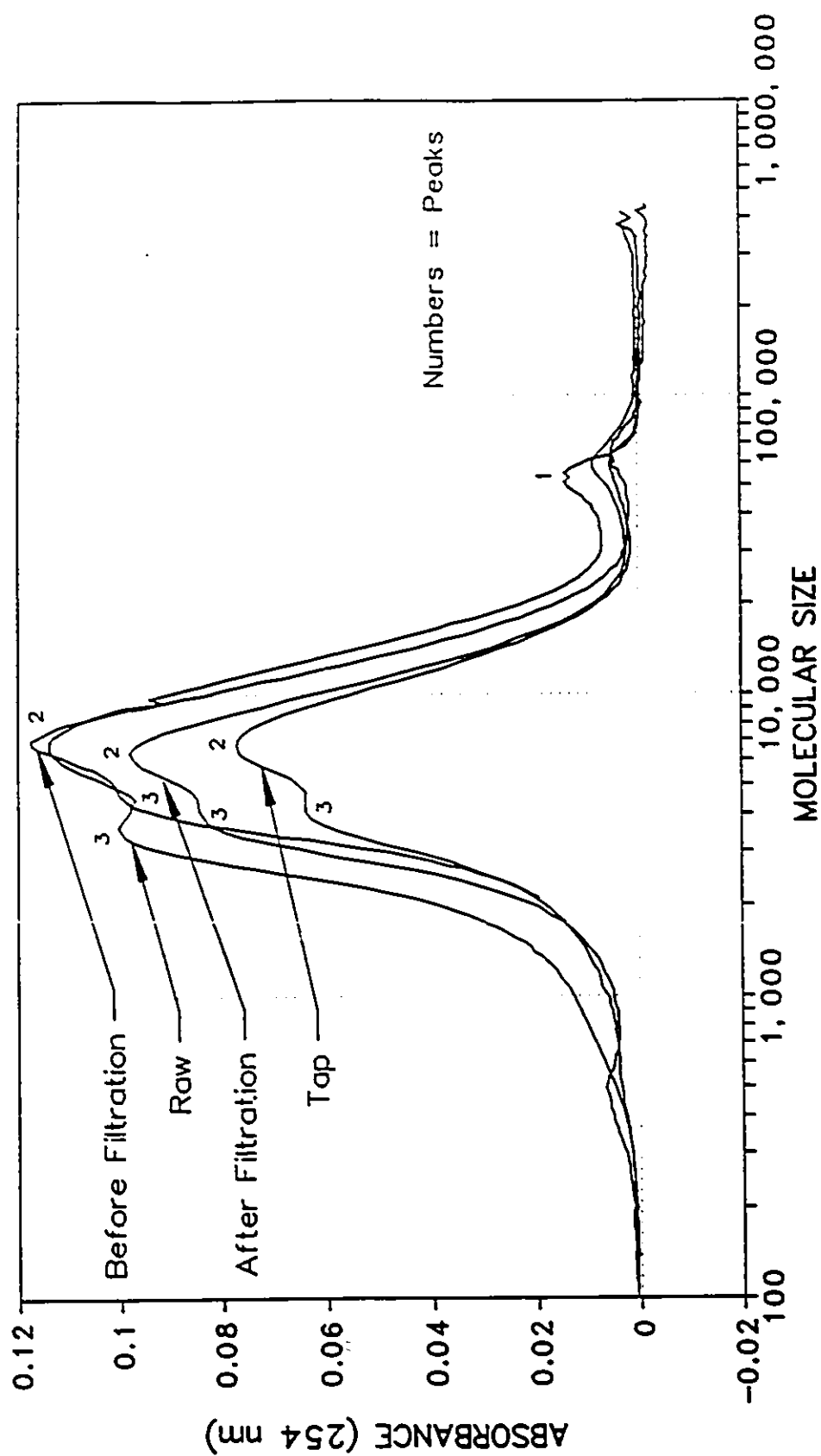


Figure A.11. GPC-AMSD of humic substances, July 1992.

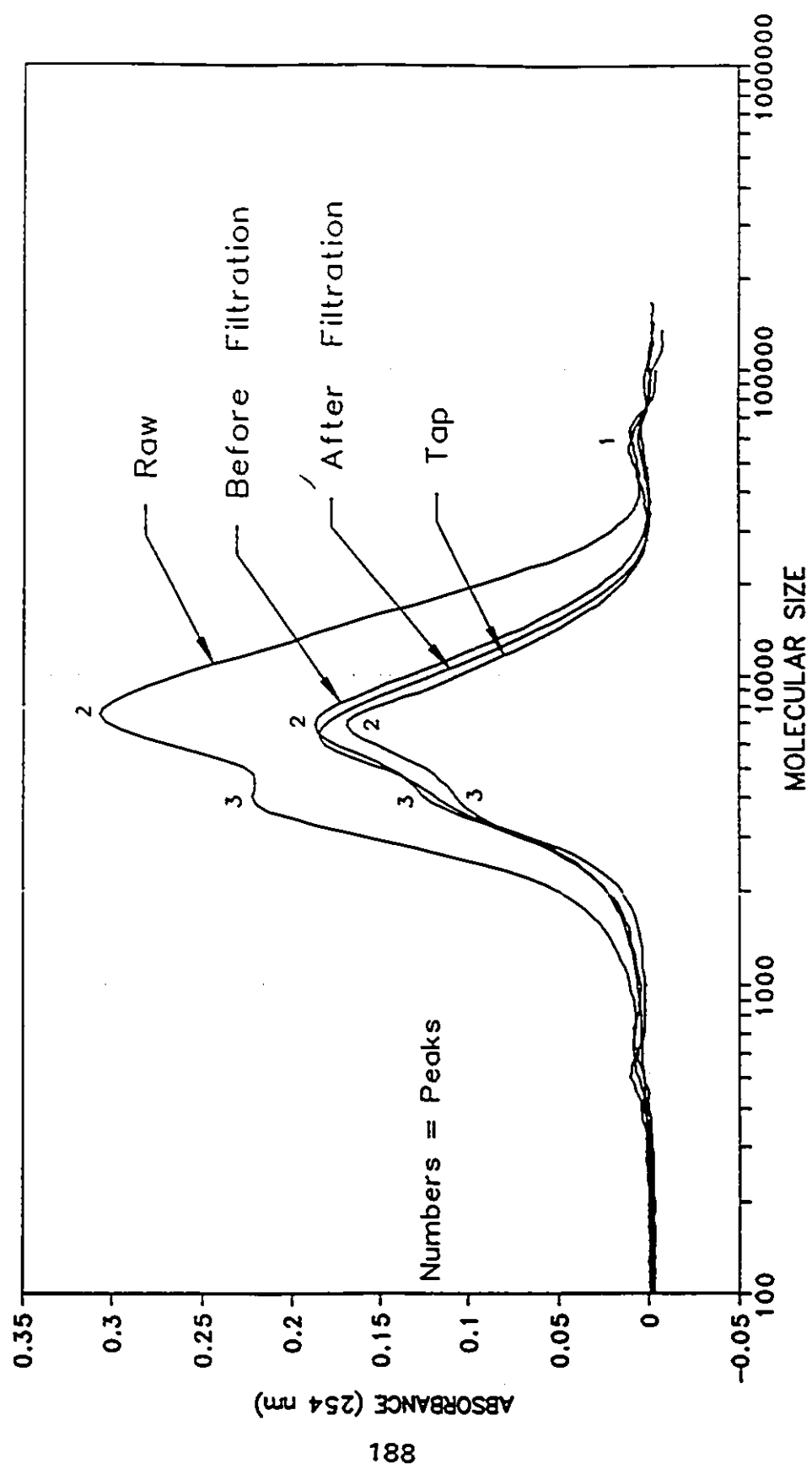


Figure A.12. GPC-AMSD of humic substances, August 1992.

VITA AUCTORIS

Name:	María Teresa Alarcón-Herrera	
Place of birth:	Tepehuanes, Durango. México.	
Date of birth:	December 3 of 1955	
Education:	1973	High School Certificate. Durango Technological Institute. Durango City, Dgo. Méico.
	1977	Bachelor of Sciences. Industrial-Chemical Engineering. Durango Technological Institute. Durango City, Dgo. México.
	1979	Advanced Studies Diploma D.E.A. <i>Industrial Chemistry The Water and its Pollutants</i> . National Institute of Applied Sciences. Toulouse, France.
	1982	Master of Engineering. Environmental Engineering. National Autonomous University. México City, México.
	1985- 1986	Advanced Studies. Institute of Wastewater. University of Hannover. Germany.
	1989- Date	Ph.D. Candidate. Environmental Engineering. University of Windsor, Ontario. Canada.
Professional Experience:	1977- 1978	Celulosicos Centauro. Process Engineer. Durango City, Dgo. México.
	1979- 1984	Mexican Nuclear Regulatory Commission. Systems evaluator engineer. México City, México.

1986- Electrical Research Institute. Research Engineer. Cuernavaca,
1988 Mor. México.

1989- University of Windsor. Research and Teaching Assistant.
Date Windsor, Ontario. Canada.

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